PETROLEUM REFINER

SPECIALIZED FOR THE OIL REFINING INDUSTRY, INCLUDING PETRO-CHEMICAL ENGINEERING, PETROLEUM SYNTHETICS AND NATURAL GASOLINE

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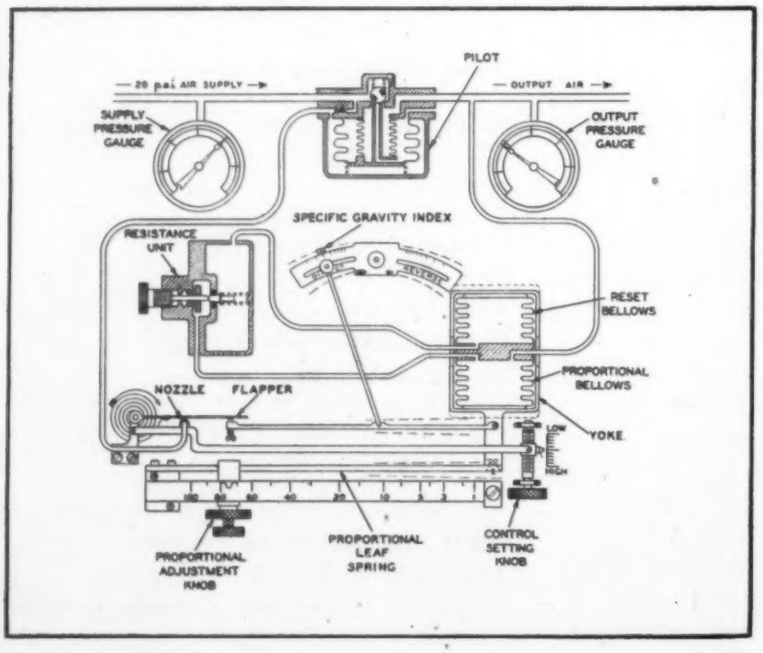

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A GULF PUBLISHING COMPANY PUBLICATION

THE LOOK BOX

THOSE disposed to calculate the disaster that will come with exhaustion of oil reserves should catch some comfort from the chemical and mechanical acrobatics to which gas and coal are being subjected. In the pilot plant it long has been known that methane can be converted into motor fuel. Now commercial-scale plants are assured wherein this will be done in quantity and along with the motor fuel will be produced diesel fuel, several impure alcohols and hydrogen.

In Case Of Worry

The processing of methane means that the petroleum reserve has been doubled since on a quantity basis the natural-gas reserve equals crude oil and in recent years oil-field discoveries have been in favor of hydrocarbons in the gas state.

More recently some experiments, fostered by the railway interests, have been successful in burning coal in an internal-combustion engine. The coal is powdered to talcum mesh and injected along with required atmosphere. It is true that this is only a successful experiment, still it can be accepted that coal will become a fuel for internal combustion, a status which will place coal in competition with diesel fuel.

Furthermore, coal so prepared can be burned for home heating, thus placing it in a better competitive position with furnace fuels.

But this development in coal takes on its highest promise when it is realized that by gasification it becomes a raw material for motor fuel, diesel fuel, as well as other products now had from crude oil. And coal at the mine can be pulverized to talcum mesh and transported through pipe lines, just as oil and natural gas are now economically transported.

The coal beds of this nation are within such easy reach that ownership of oil can anticipate the competition. If the keepers of public welfare do not appreciate this significant development, some convincing methods of presentation should be found.

Exhaustion of the oil reserves of this nation is so far removed that worry is not in order. What may justify some concern is the fact that natural-gas conversion is a reality and one that can influence the value of crude oil. And but little further back is the prospect of doing so many things with coal that both gas and oil have no assurance of long dominance.

IT IS to be hoped that the petroleum industry can function permanently under open competition. Only fair competition can establish fair prices. Whatever the claims of its administrators and the hopes of those who favor it, OPA is in effect an effort to favor an element of the population with unfair prices. The fixing all too often favors the buyer rather than the seller.

Fair Prices

In open competition prices are fair and can be of no other order. If under it too much oil is refined, some will sell it at lower prices in order to balance inventory. If in time too little oil is refined, prices will advance, as they should. Whatever the price it will be fair if there is competition.

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The price may not be what the buyer would like but it will be fair, and that is essential in a free economy.

Without this freedom of play in price fairness fades from buying and selling. When a board determines price it must ignore economic influences, which are beyond prediction. Consequently its fixed prices favor either buyer or seller and fairness ceases to exist.

Already the petroleum industry has given heed to free competition. An increase in the price of crude oil came in July without scrutiny of any bureau in Washington. In time that increase in raw-material cost will be reflected in finished-material cost. If supplies are not excessive the whole price structure in petroleum will increase. When and if supplies become excessive prices will drop.

It is vital to assure open competition. With that competitors will restrain each other and fair prices will exist.

Fuel Oil Leading

ANALYSIS of the increasing consumption of oil shifts the spot light to fuel oils. Motor fuel has for so long been a leader that it seems peculiar to learn that for 1946 when total consumption will be 20 percent higher than 1941, motor fuel will increase but 10 percent, while residual fuel oil will increase 25 percent and distillate fuels will increase 42 percent.

The estimate is by the United States Bureau of Mines, whose studies indicate that for 1946 total requirements of all oils will be 5,223,000 barrels daily. In 1941 the requirement was 4,359,000 barrels daily.

Encouragement In Rubber

THE most encouraging part of the report of the federal inter-agency policy committee on rubber, made July 28, was this paragraph:

"It is quite possible that cost and quality improvements may be such as to enable synthetic rubber to compete in a free market with natural rubber after the latter is again in ample supply."

In its recommendations to Congress the group, headed by William L. Batt, urged that subsidies be provided and that compulsory use of synthetics be mandatory only in the instance of national defense. Its recommendations were, therefore, not put forth for action by Congress, since there is possibility that the synthetic industry will maintain itself through competition.

Another wholesome recommendation to Congress was that agreements to swap information be terminated as soon as possible, as a means of stimulating private research; also that the government offer its $75,000,000 worth of plants on the market as soon as indications are that private industry will bid enough to assure maintenance of a strong industry.

Chemical rubber offers so many advantages that it seems logical to expect it to maintain itself in competition with the natural product. Butyl rubber, incidentally wholly a petroleum product, gives every promise of supplanting natural rubber for inner tubes. Other chemical accomplishments in elastomers are of such superior quality that their expanding use is certain.

Thus far, unfortunately, chemical rubber has not matched natural rubber for casings. Since this is our foremost need, the industry must stress its research if the nation is to be certain of adequate rubber regardless of military disasters and closing of sea lanes.

Not By Consent

WHEN the Department of Justice revived the suit against 366 oil companies and the American Petroleum Institute in May its legal representatives shortly got around to the proposal that a "consent decree" be accepted, something the department could accomplish easily during the war period. For once the industry began fighting back.

Instead of a negotiated settlement, which is cheaper, the oil companies now have demanded that the government set forth some instances of actual violation of the anti-trust statutes by specific companies. The suit simply charged violations without specifying instances, thus earning the designation of "mother hubbard indictment," since it covered everything and touched nothing.

Now a motion has been filed by the oil companies asking that the government be required to file an amendment stating each claim of alleged violation ... and specifying in a bill of particulars which defendant is claimed to have done what and when and where. Furthermore each company reserved the right to be heard through its own counsel on the motions.

Evidently winning an anti-trust suit against the petroleum industry is going to reach the status of proof at least. During the war all the government had to do was to get an indictment. Rather than consume time and effort in litigation the practice was to clear matters with a "consent decree," wherein the industry admitted nothing.

In a news release Sun Oil Company stated this change in attitude as:

"Sun Oil Company demanded that the government specify with whom it alleges the company had conspired, when and where and precisely upon what matters."

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THE Synthine PROCESS

1. INTRODUCTION,

SYNTHESIS GAS PRODUCTION AND PURIFICATION

JOHN C. LANE
Gulf Research & Development Company
and
B. H. WEIL, Georgia School of Technology

IN this series of four articles on The Synthine Process, a term adopted by the authors to designate all variations of Fischer-Tropsch processing, Petroleum Refiner will present a complete summary of both history and development of this important process for hydrocarbon synthesis.

Part II to be printed in the September issue will deal with Catalytic Synthesis Reactions, and Part III will include Products, By-Products and Special Topics; Part IV will deal with Economics and Current Developments.

B. H. Weil is now chief of the Technical Information Division of the State Engineering Experiment Station, Georgia School of Technology, Atlanta. Until recently he was head of the Information Section, Chemistry Division, Gulf Research Development Company, a post now held by John C. Lane, co-author of the series.

Weil received his master's degree in chemical engineering at the University of Wisconsin after doing undergraduate work at the University of Missouri. Lane is a chemical engineering graduate of the University of Rochester. During the war, one of his assignments was preparation of abstracts of reports issued by the Technical Advisory Committee.

PETROLEUM is the life blood of the nation, both in peace and in war. Automobiles, trucks, tractors, airplanes, and ships depend upon it for motive power, and it is increasingly used to supply energy and heat to homes and industries. Its use and importance in World War II were far too great and too recent to require description here.

The peacetime utility and wartime indispensability of petroleum have induced economists, business men, scientists, and the general public alike to view with decided interest all of the facts and controversies over the extent of future supplies. No decision in this argument has yet been reached, nor is it fitting here to attempt to derive one. What does seem clear, however, is that: (1) domestic peacetime petroleum demand will continue to rise; (2) domestic costs of exploration and discovery will continue to increase; (3) any near-future war will require vast quantities of petroleum both in the field and at home, where shortages nearly caused a breakdown during the recent conflict; (4) nuclear (atomic) energy will probably first be utilized to provide power and heat on a large scale for industries and communities, its use to motivate ships, trains, and giant aircraft coming only after a number of years, and perhaps never for automobiles as we know them[36]; and (5) solid fuels, unforeseen developments aside, will never be as convenient for certain uses as are the products of petroleum.

Many economic factors will continue to play their part in the future scene. Rising domestic petroleum prices may cause some shifts to other fuels, unless the price increase is checked by a flood of foreign oil. Users of petroleum products will be provided with more efficient equipment. Conservation pressure plus higher prices may cause the widespread use of destructive hydrogenation of heavy residues and low-grade crudes, thus lessening the required ratio of crude oil to gasoline.

Several petroleum economists have forecast petroleum demands for the next decade, or even longer, using premises which are sound and logical as far as past experience can foretell. All of these forecasts agree that these demands will call for such vast quantities of oil that production will have to be materially increased or imports expanded. Considering these circumstances, there is little wonder that much attention is being given to the subject of petroleum substitutes. A great part of this interest is being directed toward the use of the Synthine process—the production of synthetic petroleum products by the catalytic hydrogenation of carbon monoxide.

The Synthine Process

The Synthine process is of particular interest because its raw materials, hydrogen and carbon monoxide, can be obtained from many substances in many ways. In particular, they may readily be derived from natural gas or coal, the first material offering decided economic advantages in this country and the second providing assurance that reserves are almost inexhaustible.

Gasoline and other "petroleum" products have never been produced commercially by the Synthine process in this country, but plans for the first full-scale plant, using natural gas, have virtually been completed,[16, 21, 118] and the plant may even be in operation before 1948. In Europe, however, the "Fischer-Tropsch" process has been in actual use for over a decade, and it has been said that only inter-

company rivalry prevented it from playing as important a role in Germany during the recent war as did the hydrogenation of coal.[17]

History

The fact that a hydrocarbon (methane) could be catalytically produced from carbon monoxide and hydrogen was early observed by Sabatier, and in 1913 the Badische Anilin- und Soda-Fabrik revealed that mixtures of higher hydrocarbons and oxygenated compounds could be catalytically produced from a similar mixture under high pressures.[166] Ten years later, Franz Fischer and Hans Tropsch, who had noted similar results in work with an alkali-iron catalyst at 750-840° F. and 100-150 atmospheres pressure,[49] observed that increasing yields of hydrocarbons were obtained as reaction pressures were lowered and that these compounds definitely predominated at pressures lower than seven atmospheres. More active catalysts were required to increase yields, however, since these fell rapidly with the decrease in pressure, and it was not until 1925-26 that the discovery of suitable catalysts for a process operated at atmospheric pressure and 482-572° F. was announced.[50, 167]

The chemical mechanism of the Synthine process has been the subject for much debate, some of which will be given in detail in a later article. According to one of the current theories[90, 140] the catalyst must serve a dual function—hydrogenation and polymerization; and other functions, such as isomerization and perhaps even cracking, may be required of future optimum catalysts.

The process was put into commercial operation in Germany in 1936, and by 1940 the annual production showed a tenfold increase. France, Japan, and Manchukuo also erected plants, and the process received intensive study in England and in this country. One phase of the present $30,000,000 synthetic liquid fuels program of the Bureau of Mines deals with the Synthine process as an outgrowth of some of the bureau's early research, and many domestic petroleum and coal companies have engaged in even more intensive studies.

Nomenclature

It seems timely here to dispel some of the confusion which the use of different terms for the process appears to have engendered. The term, "Synthine," is one which has gained much favor in this country in recent years, primarily because it is a contraction of the words "*synth*etic" and "gasol*ine*." It is true that such a coined word could be applied, if desired to any synthesized gasoline, and that other "petroleum" products are also produced by the reaction. However, the term has the added advantage of being the Anglicized form of the German "Synthin," a contraction of "*synth*etisches Benz*in*," the term which the Germans have long applied to the process and its chief product.

The mixture of hydrocarbons and oxygenated compounds obtained by Fischer and Tropsch in their early work was given the name "Synthol," and this term is currently being applied to a version of the process developed in this country by one engineering concern.[121] This use may be (1) a carry-over from early days of cooperation with German interests, or (2) the process used may actually resemble the original "Synthol" method and produce oxygenated compounds in addition to hydrocarbons. The second premise is rendered plausible by the fact that press releases by this company have discussed oxygenated compounds as by-products. No detailed technical information has yet been published. In any case, the term "Synthol" is far from being sufficiently representative for general application.

Considerable use has been made of the term "Fischer-Tropsch" process, for obvious reasons. This is perhaps fitting, since the basic contributions of these men are beyond refutation. However, the variations of their process are now so numerous that many companies do not particularly care to designate their methods by this term.

Certain other German terms are not likely to dominate the domestic scene but are of importance because of their frequent occurrence in the literature. In Germany, where the process depends chiefly upon coal for the preparation of the synthesis gas, it was fairly logical to give the products the coined name, "Kogasin," derived from the German words for coal, gas, and gasoline (*Ko*hle-*Gas*-Benz*in*). "Kogasin I" was the title applied to the naphtha fraction (boiling from 86-392° F.), while the term "Kogasin II" was used for the heavier hydrocarbon products (gas oils, diesel fuels, etc.). These terms would certainly be inappropriate in the United States, where natural gas almost certainly will prove to be the preferred raw material for the process.

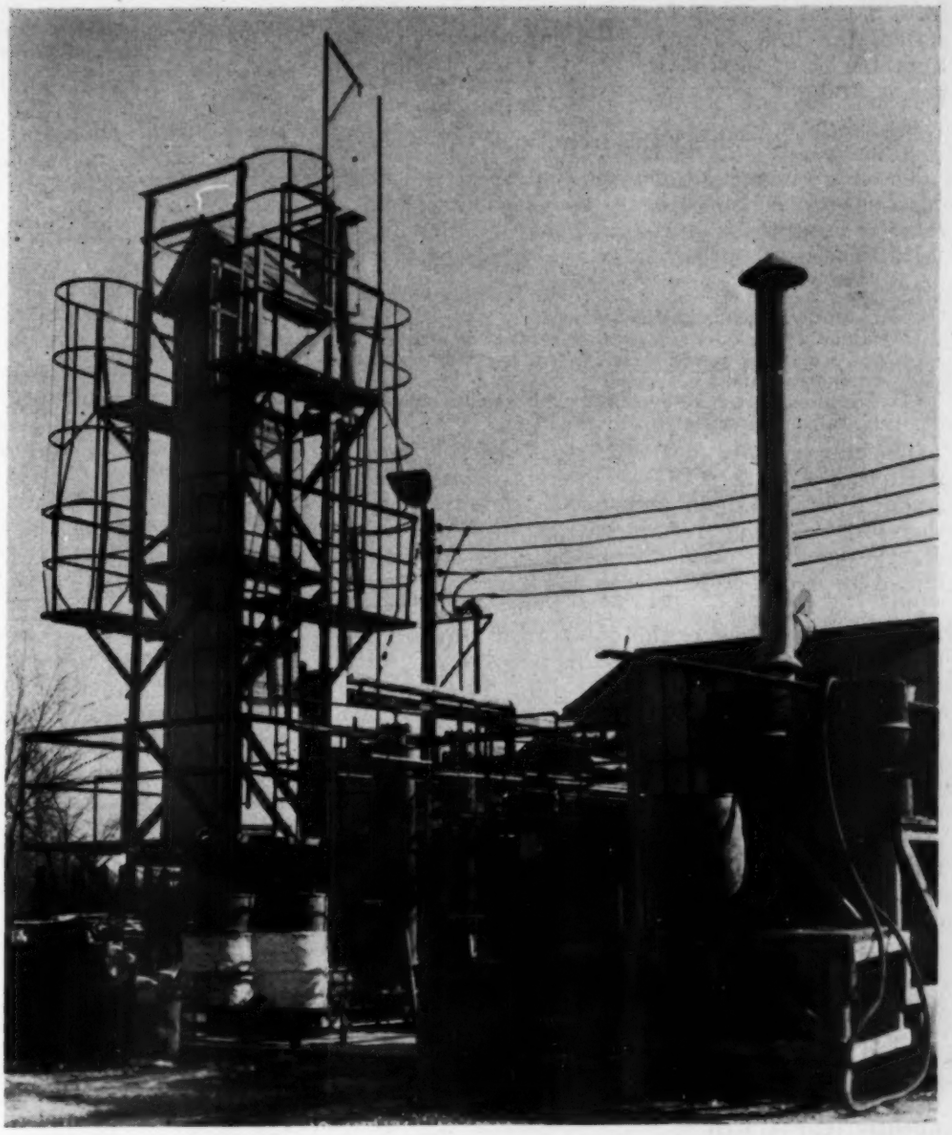
It seems likely, then, that the term "Synthine," possibly uncapitalized, will become increasingly associated with the many variations of the hydrogenation of carbon monoxide to yield petroleum-like products. The word may be also applied to the products of the synthesis—Synthine gasoline, Synthine gasoil, etc.—which products, in turn, may be generally classed as "Synthinates." "Synthine" appears to be a much less unwieldly term for the process than the awkward (and not sufficiently inclusive) title "the indirect hydrogenation of coal."

Purpose of Series

In the course of the authors' work in the field of petroleum refining, they have had occasion to prepare several surveys of the literature and patents on the Synthine process, covering the subject in as exhaustive a fashion as facilities permitted. This series has been prepared in an attempt to correlate the more significant facts into a coherent whole and, at the same time, to present a representative bibliography for further study. Space prohibits inclusion of all of the some 3000 related articles, books, and patents which were identified in these surveys. However, more than enough have been used to authenticate the information presented.

Since the literature on the Synthine process is so copious and its phases are so diverse, adequate treatment requires several articles. The subject matter appears to fall fairly logically into the following four categories: (1) production and purification of the synthesis gas, (2) catalytic synthesis reactions, (3) description of products, by-products, and derivatives, in addition to various special topics, and (4) discussion of economics and current developments. This series, therefore, will consist of four articles, each of which will consider one of the above divisions.

Little further in the way of an introduction seems necessary. It might be mentioned that the Synthine process offers almost unlimited possibilities for the manufacture of synthetic aliphatic chemicals, and, in conjunction with coal hydrogenation, which yields largely aromatics, makes possible synthesis of almost



Synthesis gas pilot plant unit, using natural gas.

Photo Courtesy
Phillips Petroleum Company

any organic compound from "coal, air, and water." In regard to its possibilities as a substitute for petroleum, it is certainly interesting to note the general belief that variations of the Synthine process, using natural gas, will be competitive with petroleum at present or near-future prices, and that even the eventual use of coal will not add more than three or four cents per gallon to the cost of gasoline so produced.

Natural gas reserves, of course, are far from inexhaustible, and the ultimate reserve of perhaps 300 trillion cubic feet may have to be largely allocated to such other uses as are peculiar to its physical form. However, considerable quantities will probably be available for conversion to Synthinates for a number of years—until other demands or approaching depletion of supplies result in uneconomic increases in price.

Coal reserves, on the other hand, are sufficient to last for 3000 years at the present rate of consumption—to produce as much as 6000 billion barrels of gasoline in the extremely unlikely event that all would be converted into gasoline. New methods, also, may render coal an increasingly economic material for the Synthine process.

Synthesis Gas—Composition and Source

Depending upon the catalyst used in the synthesis reaction, the conditions of operation, and the products desired, the optimum ratio of hydrogen to carbon monoxide in the synthesis gas used in the Synthine process ranges from about 2 to 1 to less than 1 to 1. The standard synthesis with cobalt catalyst usually requires the former ratio, while the so-called "iso-synthesis," carried out over catalysts containing zinc oxide, aluminum trioxide, and thoria, uses a ratio of about 1 to 1.2.[63, 64] Although the direct hydrogenation of coal requires hydrogen of at least 92 percent purity, the Synthine process is reported to operate satisfactorily on gases containing as much as 10-12 percent of inerts (carbon dioxide and nitrogen).[132]

Theoretically at least, any carbonaceous material which can be decomposed to hydrogen and carbon monoxide can be used in the production of synthesis gas, but as mentioned, only coal and natural gas have thus far appeared of commercial interest. European operations have necessarily utilized coal because of the insufficient quantity of natural gas available on the Continent. It is generally believed, however, that synthesis gas can be prepared more economically

from natural gas than from coal; and, as previously stated, the first commercial-sized, privately-owned Synthine plant in the United States reportedly will use natural gas as its raw material.[20, 23, 118, 141]

Synthesis Gas from Coal

The more important, commercially-practical methods for producing hydrogen- and carbon monoxide-rich gas mixtures from coal include the following:

(1) Manufacture of water gas from coke in standard water-gas sets;
(2) Manufacture of water gas from low-volatile coal in more or less standard equipment;
(3) Manufacture of water gas from coal or coke using oxygen in the steam blast; e.g., in Winkler and Lurgi equipment; and
(4) Conversion of coke-oven gas with steam, either catalytically or noncatalytically.

The theoretically ideal water-gas reaction may be written: $C + H_2O \rightarrow CO + H_2$. Approximately equal amounts of hydrogen and carbon monoxide might therefore be expected from practical utilization of the reaction. Typical compositions of gases actually obtained by the processes mentioned above are given in Table I.

In order to convert the gases from any of these processes into synthesis gas, it is necessary to adjust the hydrogen-carbon monoxide ratio to the desired value, usually about 2 to 1. In the case of water gas, this may be accomplished by the well-known water-gas-shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$. A catalyst is required in this reaction, the usual one consisting of ferric oxide promoted by the oxides of chromium, calcium, and magnesium.[26, 27] Partially reduced cobalt oxide[151]; cobalt catalysts containing about 38 percent of copper[135]; magnesia and zinc oxide promoted with potassium oxide[104]; catalysts composed of active carbon and magnesia[126]; and nickel catalysts promoted with a variety of non-reducible oxides, preferably magnesia,[32, 144] have all been proposed as shift catalysts. The carbon dioxide formed in the shift reaction may be removed by compressing the gas and scrubbing it with water or by reacting it with ethanolamines, which are subsequently regenerated.[129]

Coke-oven gas, while rich in hydrogen, contains relatively little carbon monoxide, considerable methane, and some unsaturated hydrocarbons, chiefly ethylene. These hydrocarbons may be converted to hydrogen and carbon monoxide by reacting the coke-oven gas either catalytically or noncatalytically with steam. Catalysts suitable for the reaction are those later specified for the production of synthesis gas by the "methane-steam" reaction. From 100 volumes of coke-oven gas of the composition given in Table I, it is said to be possible to obtain 190 volumes of converted coke-oven gas of the following composition: CO_2, 4.2 percent; CO, 16.3 percent; H_2, 75.3 percent; CH_4, 1.0 percent; and N_2, 3.2 percent.[129] In this gas, the ratio of hydrogen to carbon monoxide is too high, in contrast to water gas in which it is too low. However, mixture of the 190 volumes of converted coke-oven gas with 250 volumes of water gas made from coke in a standard water-gas set (composition in Table I) would yield 440 volumes of synthesis gas of the following composition: CO_2, 4.6 percent; CO, 30.4 percent; H_2, 60.9 percent; CH_4, 0.7 percent; and N_2, 3.4 percent. "An alternative method of operation is to blow the water-gas generator with a mixture of steam and coke-oven gas (10 cubic feet of coke-oven gas per pound of steam), whereby synthesis gas is produced in one stage."[129] Blowing the generator

TABLE 1
Typical Compositions of Gases Produced from Coal or Coke by Various Methods (129, 132)

Charge	Coke	Low-Volatile Coal	Coke	Coke	Non-Coking Coal	Coal
Method	Water-Gas	Water-Gas	Water-Gas	Water-Gas	Water-Gas	Coke Oven
Equipment	Standard	Standard	Winkler (O_2+H_2O)	Winkler (O_2+AIR +H_2O)	Lurgi (O_2+H_2O)	Coke Oven (Debenzolised)
Gas Composition:						
CO_2	5	3.8	13–20	15.2	30	3.0
CO	41	39.7	47–36	32.9	20–15	7.0
H_2	50	54.1	39–41	29.7	30–35	55.0
CH_4	0.5	0.7	0.6–0.4	1.3	15–20	27.0
N_2	3.5	1.5	0.4–0.5	20.9	2.0	6.0
C_nH_m	.....	0.2	.....	.....	.....	2.0

with a mixture of steam and coke-oven gas either alternately with steam-oxygen blasts or continuously in admixture with oxygen has been claimed in several patents.[162, 163, 176]

German Methods

Recently released information obtained by the United States Technical Oil Mission in its survey of German synthetic gasoline plants illustrates the various methods and combinations of methods the Germans were using to produce synthesis gas from coal. This information has revealed that the majority of the commercial-scale German plants made their synthesis gas from coke by means of the water-gas reaction, followed by a catalyzed water-gas-shift to obtain the desired ratio of hydrogen to carbon monoxide. The German water-gas-shift catalyst is said to have analyzed 38.5 percent Fe_2O_3, 18.2 percent CaO, 5.4 percent Cr_2O_3, and 5.2 percent MgO, with minor amounts of other constitutents, including 18.0 percent water, differing little from that commonly used for the reaction.[26]

The cracking of coke-oven gas was utilized in a number of the German plants in order to produce a hydrogen-rich gas for admixture with water gas, thus minimizing the amount of water gas subjected to the shift reaction. As an example of such a combination of synthesis gas processes, the synthetic gasoline plant of Steinkohlen-Bergwerk Rheinpreussen at Moers-Meerbeck (near Hamburg), Germany, manufactured about 41,000,000 cubic feet of water gas daily in 11 standard Koppers[114] water-gas generators. About 18 percent of the water gas (about 7,400,000 cubic feet per day) was then passed through a shift apparatus with normal shift catalyst to increase its hydrogen content. Approximately 353,000 cubic feet per hour (about 8,500,000 cubic feet per 24-hour day) of coke-oven gas were "cracked" noncatalytically with steam at about 2200° F. in six Cowper stoves to bring the hydrogen-to-carbon monoxide ratio up to 2:1, which was the desired ratio at that plant.[27]

Several less conventional methods of making synthesis gas were in operation in some German synthetic gasoline plants. At Wanne-Eickel, the Krupp-Lurgi process for the manufacture of low-temperature coke was employed to make a coke which, when used in water-gas sets, gave blue water gas with a hydrogen-carbon monoxide ratio of 1.35 to 1, this ratio being nearer that required for synthesis gas than that of water gas manufactured from high-temperature coke.[26, 66]

The Pintsch-Hillebrand process for the complete gasification of brown coal or other non-coking coals to either synthesis gas or hydrogen was reported to provide the necessary heat for the water-gas reaction by passing steam and previously-formed water gas

through regenerators heated in alternate cycles by combustion of producer gas.[26, 110]

The Schmalfeldt-Wintershall process for the manufacture of synthesis gas from non-coking coal was said to have been under large-scale development when the war began. This process is said to be indifferent to the moisture and ash content of the charge, and thus particularly suited for use on run-of-mine coals.[63] In the original process, very finely-pulverized coal was first dried in a stream of hot recirculating gas, removed in a cyclone separator, and fed into a generator with a hot stream of recirculating gas containing sufficient makeup steam for complete gasification, a portion of the recycle stream being continuously withdrawn as synthesis gas. Interrogation of German technical men is reported to have revealed that a number of difficulties were encountered in commercial operation of the process, however.[123] Plans for the revision of a large installation built by Wintershall A.G. at Luetzkendorf in central Germany were revealed in a document found at Leuna in I. G. Farbenindustrie's possession.[26] Lack of gas-producing capacity was said to be one of the shortcomings of the process. According to interrogated Germans, increased capacity was obtained by installing a new type of rotating-grate generator and adding oxygen in relatively small amounts to increase the heat available for gasification. Since the gas from this process contained only 76 percent hydrogen plus carbon monoxide, the plant would have required 4,000,000 cubic feet per hour of synthesis gas in order to produce 82,500 short tons of Fischer-Tropsch product per year. Four generators, plus one spare, were needed to produce this quantity of gas. About 4,325,000 cubic feet per hour of producer gas were required for heating purposes, and about 49,500 cubic feet per hour of oxygen for addition to the generator. Approximately 50 pounds of brown coal (dry basis) were required to make 1000 cubic feet of synthesis gas by this method.[26]

The raw-material requirements of the various generators vary according to the type and efficiency of the installation. The standard-type Koppers generators used in the Steinkohlen-Bergwick plant at Moers-Meerbeck charged about 981 metric tons per day of coke containing 82.6 percent carbon and volatile matter, 8.2 percent water, and 9.2 percent ash in order to obtain a daily output of 1,146,070 cubic meters of water gas.[110] In English units this is approximately 53.5 pounds of coke per 1000 cubic feet of water gas.

Winkler generators[72] charge lignite, coal, or semi-coke reduced to a particle size of about ¼ inch. Oxygen and steam; or air, oxygen, and steam are added in such a way that fuel is kept in a constant state of agitation. The composition of Winkler water gas from coke both with and without air in the oxygen-steam stream is given in Table I. Raw material consumption per 1000 cubic feet of gas is as follows[132]:

	Oxygen + Steam	Oxygen + Air + Steam
Coke, pounds	40.9	33.0
Air, cubic feet		242
Oxygen (98 percent), cubic feet	284	179
Water, pounds	19	13.2

Winkler process plants in actual German use were said to be superior to Schmalfeldt process plants, although a properly-designed plant using the latter method was thought to be economically superior.[123]

The Didier gas generator,[137] which charges ¼- to 1-inch briquets of bituminous coal or lignite, is a combination of a vertical retort and a water-gas generator, both being operated continuously. A gas suitable for use in the Synthine process is obtained from the apparatus by *in situ* conversion of the distillation gas which is then blended with the water gas simultaneously produced in another zone. A part of the heat requirement of the process is said to be supplied by the sensible heat in the off-gas, and the remainder by the heat of reaction of the subsequent catalytic synthesis. The thermal efficiency when using lignite briquets is claimed to be 75 percent.[132]

The Lurgi process for complete gasification of various solid fuels using steam and oxygen under pressure,[5, 40, 43, 69, 102, 115, 127, 152] the previously-mentioned Pintsch-Hillebrand process[3, 26, 110, 130, 131] and other processes and equipment[34, 42, 78, 105, 124, 137, 154] have all been described in the literature. Complete continuous gasification and its economic advantages have been discussed in several articles.[19, 70, 85, 149, 155] Other references on continuous gasification processes include [1, 7, 11, 39, 155]. A review on large-scale water gas production, including numerous details on the various processes, has been given by Thau.[136] A number of other articles have treated the subject at more or less length.[6, 25, 28, 46, 62, 83, 122] According to Dolch,[40, 41] the oxygen-steam processes give gas yields which are superior to those from processes in which the heat is obtained by the separate gasification of part of the fuel. He also has claimed that processes of carbonization and gasification in vertical ovens at atmospheric pressure with oxygen-steam mixtures produce a low-methane gas and require the least oxygen.

Underground Gasification of Coal

As previously mentioned, the higher cost of producing synthesis gas from coal renders it probable that commercial Synthine operations in the United States will utilize natural gas as the raw material until such time as the economic advantage is lost as a result of approaching depletion of gas reserves and the consequent higher prices brought about by competition for the lessened supply. However, the quantity of coal available for conversion to liquid fuel is vastly greater than the amount of natural gas which could be diverted to this purpose, and keen interest awaits the development of any process which can produce synthesis gas from coal at less expense than the methods now in use. The underground gasification of coal shows strong potentialities of becoming just such a process, since it gasifies the coal *in situ* and entails no costs for mining and transportation of the raw material or for gasification equipment.

Although Siemans in 1868 and Mendeleev in 1888 suggested the idea, and Betts in 1909 patented a process, there is no record of actual experimentation on underground gasification until just before the first World War, when Sir William Ramsay began investigations near Tursdale Colliery, Durham, England.[79] However, Ramsay's project was discontinued at the outbreak of the war, and no appreciable work along this line appears to have been done until after 1931 when the Soviet government decided to subsidize experiments on underground coal gasification. The Podzemgaz trust was formed in 1933, and some preliminary experimental work was done in that year. The first experimental station for the gasification of coal on an industrial scale began operation in the Donets coal field in 1937, while the first truly commercial installation went into operation late in 1940. The Third Five-Year Plan (1938-42) is said to

have called for construction of plants in the Donets and Moscow coal fields and in the Urals, Eastern Siberia, Central Asia, and the Far East. While the proposed scale of these operations is not completely known, it has been stated that the station at Lisichansk (in the Donets coal field) was expected to have a daily output of 20,000,000 cubic feet of gas with an average calorific value of 275 Btu per cubic foot. Two of the other proposed stations were to have daily capacities of 14,000,000 and 8,000,000 cubic feet, respectively.[8]

Four different methods of underground gasification have reportedly been investigated by the Russians: (1) the "chamber" method, (2) the "stream" method, (3) the "percolation" method, and (4) the "crevice" (or "borehole-producer") method. With the exception of the chamber method, which is considered obsolete, each of these processes is especially adaptable to a particular type of seam, the determining factors in the choice of the particular method usually being the seam's inclination and depth. The Russians are said to have carried out underground gasification experiments on coal seams ranging from 1-16 feet in thickness, 65-200 feet in depth, and 0°-75° in inclination.[148]

Chamber Method

The chamber method,[4,79,80,86] which consisted of isolating a panel of coal from the rest of the seam by means of brickwork walls and constructing shafts on opposite sides of the panel for the air inlet and gas offtake, was the earliest method investigated by the Russians. Two variations of the method were tried, one in which the natural fissures and porosity of the coal seam were utilized for the passage of the air and gas through the chamber, and the other in which the coal in the chamber had been previously broken up. Although the chamber method was workable, it still required considerable underground labor for preparation of the chambers and was abandoned in favor of the other three processes.

Stream Method

The stream method of underground gasification involves driving a gallery lengthwise along the coal seam to connect two shafts drilled from the surface to the level of this gallery, thus forming a panel of coal with an air inlet and a gas outlet at opposite ends. A fire is started at the base of the air-inlet shaft, the air blast admitted, and the gas taken off at the other shaft. The fire burns progressively upward toward the roof of the seam, and the ash, together with any of the unburned coal which may fall, collects in the space below the fire zone. Three zones of reaction are said to exist in the gallery of the stream method. In a test panel 7.5 meters long, their identity and extent were found to be as follows[44, 136]:

(1) The "combustion" zone, extending for about 2½ meters, in which the coal burns mainly to carbon dioxide;
(2) The "recovery" zone, extending for about 3 meters, in which the carbon dioxide is reduced to carbon monoxide and considerable amounts of hydrogen appear in the gas; and

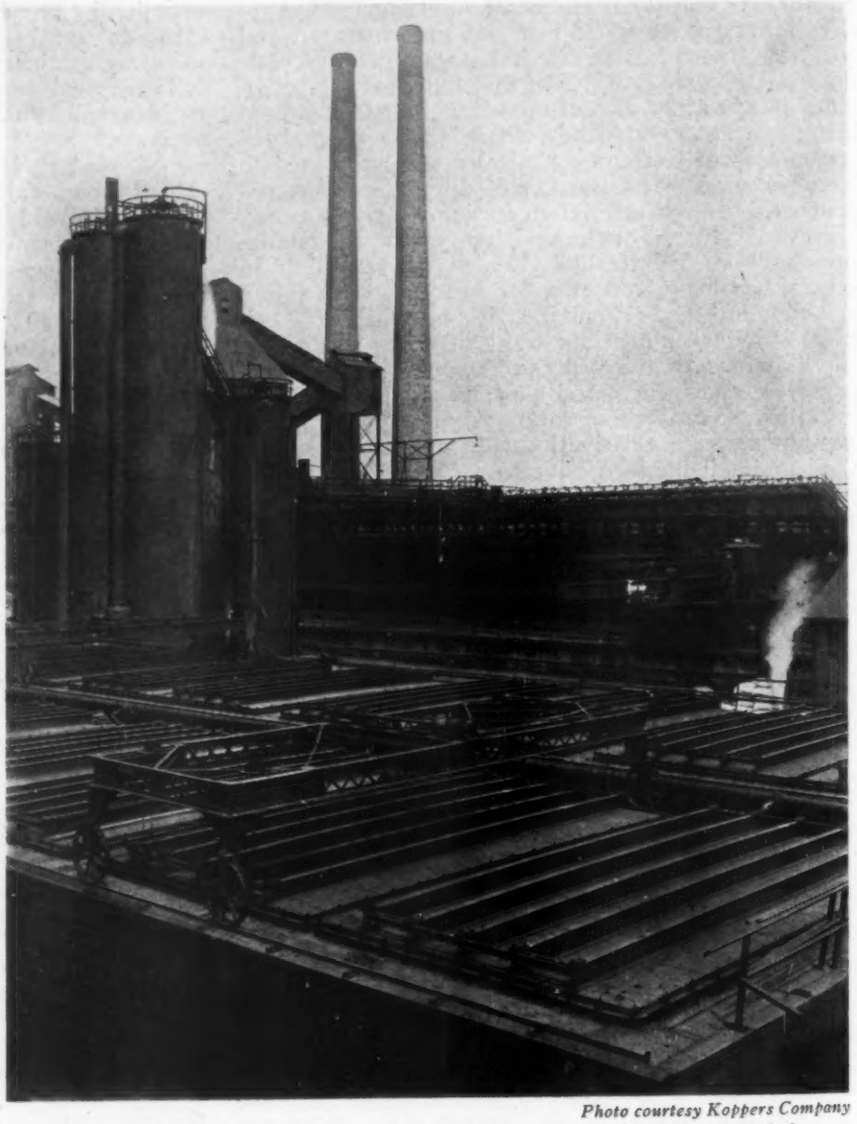


Photo courtesy Koppers Company

Iron-oxide gas purifying boxes, with towers in the background for liquid purification of the gas. This process was used in Germany for removal of hydrogen sulfide from synthesis gas.

(3) The "distillation" zone, extending for about 2 meters, in which the carbon dioxide content of the gas becomes constant and the gas is enriched by carbonization of the coal face.

The coal consumption is not equal in all three of these zones, the maximum amount being consumed in the combustion zone. Therefore, the direction of the blast is periodically reversed in order to avoid unsymmetrical burning out of the panel.

Unless steam is added to the air blast, the gas from underground gasification is deficient in hydrogen as regards normal synthesis-gas requirements. A regenerative variant of the stream method, in which air and steam are blown for 20- to 30-minute periods alternately in opposite directions, is said to produce a

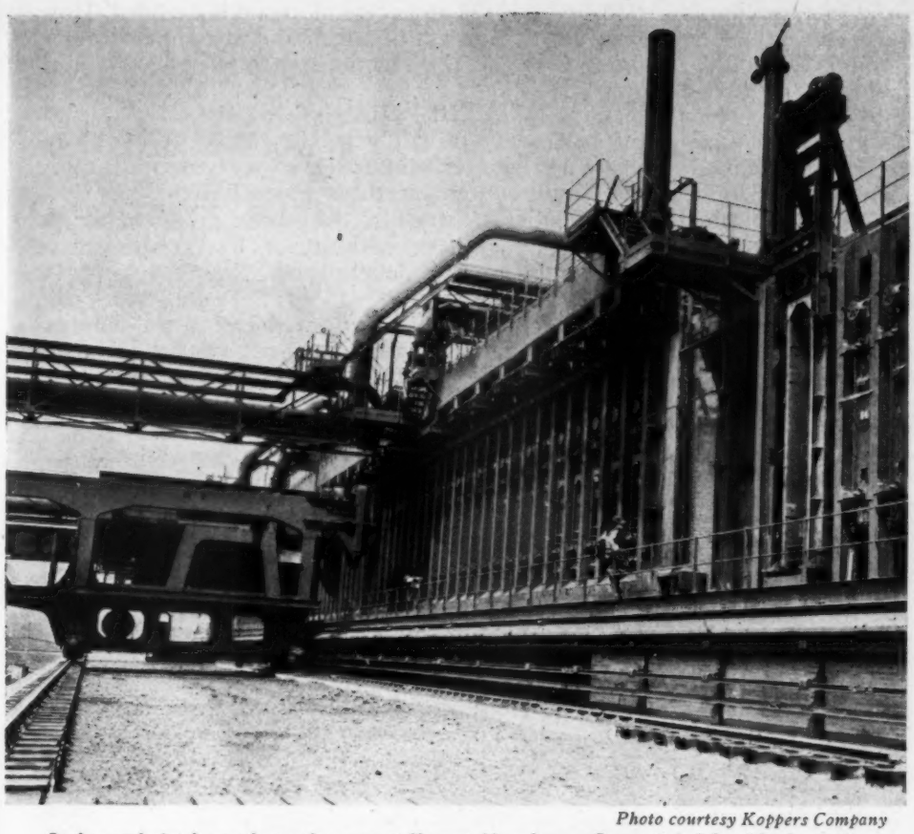


Photo courtesy Koppers Company

Becker underjet by-product coke oven at Kearny, New Jersey. Conventional Synthine operations based upon coal use coke as raw material.

water gas of the following composition[33]:

CO_2	15 percent
CO	26 percent
H_2	53 percent
CH_4	0.7 percent
O_2	0.5 percent
N_2	4.8 percent

The stream method requires a fairly small amount of underground labor, and by directional drilling it is conceivable that the gallery as well as the shafts could be drilled from the surface, since it is by no means essential that this gallery be perfectly horizontal. Another proposed design for an underground gas generator consists simply of two shafts drilled from the surface in a V-shape, one to serve as air inlet and the other as gas outlet, the fire being built at the intersection of the shafts.[18] The stream method is particularly suited to steeply inclined seams. In horizontal or only slightly inclined seams, the access of air to the coal face becomes obstructed by ash and fallen, unconsumed coal.

Percolation Method

The percolation (or filtration) method, patented in 1909 [158], depends on the formation of shrinkage cracks and fissures in the coal when heated, so that it becomes readily permeable to gas. This method is particularly applicable to horizontal seams and requires no underground mining. In commercial practice, vertical holes are drilled into the seam in concentric rings spaced 20 to 40 yards apart radially. Starting-up operations consist of building fires at the bottom of the adjacent shafts, blowing air down central pipes, and collecting the gas produced, which passes up the same shaft around the central pipe. The heat from these underground fires develops cracks and fissures in the coal, so that it becomes possible for the gases in one hole to pass through the seam to the adjacent hole. As soon as this condition is established, the gas offtake of one of the holes and the air inlet of the other are sealed, and gasification of the panel between the holes is begun. When the coal between these two holes has been gasified, one of the holes is sealed off and an adjacent hole brought into use, the panels between all of the holes eventually being gasified in succession.[148]

In one modification of the percolation method, three concentric circles of vertical holes are drilled, each circle being connected at the top by headers. Air at five atmospheres pressure is blown in at the inner circle of holes and oxygen at eight atmospheres at the outer circle, the gas produced being taken off from the middle circle.[59]

A combination of the percolation and stream methods has been suggested for use in horizontal seams where the stream method fails because of collapse of the roof. The seam to be gasified is divided into squares by vertical shafts, and these shafts are connected at their lower ends by horizontal borings. The stream method is used until the horizontal borings (called "fire-drifts") become obstructed by roof falls and ash, after which gasification is continued by the percolation method, assuming that the adjacent coal has become sufficiently porous for this method.[95]

In the crevice method of underground coal gasification, three parallel shafts, each of about two feet in diameter, are drilled from the surface into the coal seam, the center shaft serving as the blast inlet and the shafts on either side serving as gas-offtake manifolds. The shafts are then connected by a series of holes of about four inches in diameter and five yards apart, so laid out that they are parallel to each other and intersect the shafts at right angles.

Various methods for constructing these shaft-connecting holes have been employed. One method, "hydrolinking," utilizes high-pressure water jets, while "electrolinking" consists of burning out the coal between electrodes placed some distance apart in the seam.[18, 148] Another method for linking the shafts employs a jet of oxygen to facilitate directional burning. Where space in the vertical shafts permits, a number of specialized drills have been developed for the purpose.[88]

The coal surrounding each of the shaft-connecting holes is gasified by starting a fire in the blast-inlet shaft at the level of the particular hole in question and carrying out combustion of that "crevice" in both directions (from the center shaft) while the other boreholes are sealed off. The crevices are ignited in succession or in small groups, so that an approximately constant rate of gas production is main-

tained and the combustion of the coal in the seam is as complete as possible.

As in the stream method, the composition of the gas obtained by the crevice method may be varied within quite wide limits by the use of oxygen and/or steam in the air blast.[8, 79, 87, 146] This method requires a considerable amount of underground work, but it has the advantage of being applicable to horizontal or slightly sloping seams in which the stream method fails because of falling roofs, and also to those seams in which the percolation method cannot develop adequte cracks and fissures in the coal between its shafts. Claims have been made that 80-90 percent of the coal in a seam can be gasified by the crevice method.[148]

The chief economic advantage said to be offered by underground gasification is the reduction (and possible elimination) of underground labor which it affords. It has been stated that the Russians have increased the average output per man from 30 tons of coal per month by mining methods to the thermal equivalent of 100-190 tons per month by underground gasification.[61, 113] Where gas is the desired product, anyway, another economic advantage is the lesser capital cost of gasification equipment; Russian experience has indicated that the cost of a complete underground-gasification station is only 60-70 percent of that of an above-ground installation. The cost of power gas produced by underground gasification is said to be about one third that of similar gas produced in ordinary gasification plants.[59] Where oxygen-enriched blasts are to be used in underground installations, it has been estimated that the cost of the oxygen plant constitutes 70 percent of the total investment and that the cost of gas produced is about three times that produced with air alone.[44]

Much of the above must be viewed as indicative rather than conclusive, since the average production of bituminous coal per man-day in the United States was 5.2 tons in 1941[120], far above the Russian average, while the use of such techniques as strip mining gives even greater man-day yields, such as 14.23 tons in 1938 In any case, the use of underground gasification appears worthy of additional attention.

Synthesis Gas from Methane

Mixtures of hydrogen and carbon monoxide may be produced from natural gas, methane from coal seams, refinery gases, low-temperature carbonization gases, Synthine residue gases, or other gases rich in methane by the following processes:[29, 65, 129]

(1) Reaction with steam, according to the equation: $CH_4 + H_2 \rightarrow 3H_2$ (—50.7 K cals);
(2) Reaction with carbon dioxide, according to the equation: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ (—60 K cals); and
(3) Controlled oxidation with air or oxygen, according to the equation: $2CH_4 + O_2 \rightarrow 2CO + 4H_2$ (+7.2 K cals).

The "methane-steam" reaction has been discussed in a number of articles.[29, 30, 37, 51, 68, 76, 77, 91, 93, 96, 107, 109, 116, 157] This reaction produces a gas which is low in carbon monoxide, but which might be adjusted to synthesis-gas requirements by blending with gas from the reaction of methane with carbon dioxide, since the carbon monoxide content of the latter is high. The two reactions may be carried out simultaneously over a nickel catalyst at a temperature of about 1350° F.[129], according to the equation

$$3CH_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H_2$$

According to various investigators, studies of the equilibrium relations of the methane-steam reaction show that, above 1500° F., it is almost entirely confined to the production of hydrogen and carbon monoxide, as long as an excess of steam is avoided. However, with an excess of steam and at temperatures of about 1200° F., the reaction tends to obey the equation[29, 92, 117, 125]

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

In the absence of catalysts, the rate of the methane-steam reaction is said to be slow, becoming appreciable only at temperatures above 2370° F.[132]

A number of catalysts have been proposed for the reaction of methane with steam, by far the greater number containing nickel promoted and supported in various ways.[29, 30, 68, 106, 109, 116, 157] Among the catalysts which have been suggested are: nickel-alumina-magnesia on active carbon at about 1200° F.[38]; nickel-thoria, magnesia, and nickel-iron at about 1470° F.[89]; nickel-magnesia[143]; 25 percent nickel, 74 percent magnesia, and 1 percent boric acid at 1500-1700° F.[175]; and nickel-alumina on clay.[109] Alumina and magnesia are considered effective activators,[68, 109] while kaolin has been suggested as a support.[109]

Cobalt [29,68] was found by one group of experimenters[67] to be greatly inferior to nickel as a catalyst for the reaction at 1650-1830° F. Using a small-scale intermittent process in which the catalyst was first blasted with a gas-air mixture and the reaction mixture was thereafter injected into the catalyst bed, they found that the most reactive and most durable catalysts consisted of nickel deposited on refractory mixtures of alumina and clay, nearly theoretical conversions being reported.

Semi-industrial-scale data on an intermittent, nickel-catalyzed process similar to the one just described showed that, at average temperatures of 860-900° C. and 10-minute conversion periods, the average composition of the gas (from natural gas containing about 87.5 percent methane) was as follows: CO_2, 9 percent; CO, 22 percent; H_2, 64 percent; CH_4, 0.8 percent; and N_2, 4.2 percent. About 0.46 part of natural gas was consumed to produce one part of gas of this composition, approximately 0.30 part actually being converted and 0.16 part being burned to supply heat.[51]

Pilot-plant-scale production of hydrogen-carbon monoxide mixtures from natural gas at 1650-1920° F. using pure nickel stampings ¼ x ⅛ inch as catalyst has been described by Storch and Fieldner.[134] The gas from this process contained about 75 percent H_2, 21 percent CO, 1 percent CO_2, and 1 percent $N_2 + CH_4$.

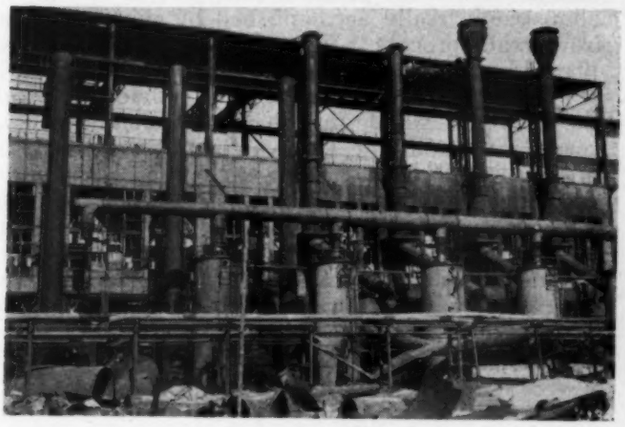
The petroleum oil-hydrogenation plants of the Standard Oil Company of New Jersey at Bayway, New Jersey, and Baton Rouge, Louisiana, reportedly use the methane-steam reaction to produce mixtures of hydrogen and carbon monoxide, utilizing the water-gas shift to eliminate carbon monoxide and obtain the hydrogen required for their operation.[31] Fairly recent improvements in the methane-steam reaction are said to include a continuous conversion process which involves addition of oxygen to the methane-steam mixture and the use of long-lived catalysts.[29,30] A recent booklet[19] gives some interesting details and estimates based on the use of propane.

Since the reaction of methane with carbon dioxide requires a reactant less readily available, generally speaking, than does the methane-steam reaction, and is even more endothermic than that reaction, less attention has been directed toward its development. However, this process does have the advantage of giving a gas unusualy high in carbon monoxide, and it therefore offers a possibility for increasing the carbon monoxide content of gas from the methane-

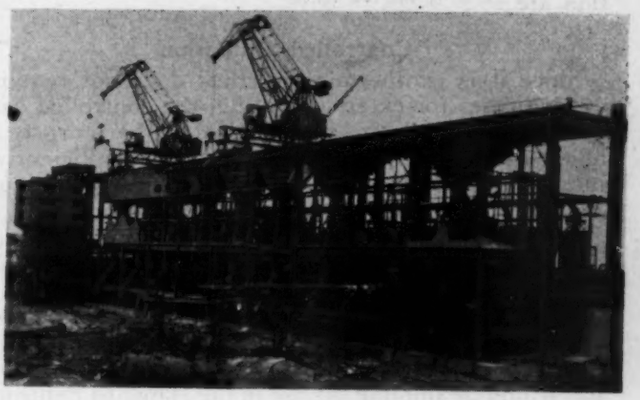
Synthesis Gas Installations in Germany After Allied Bombings

Pictures Courtesy W. C. Schroeder, United States Bureau of Mines

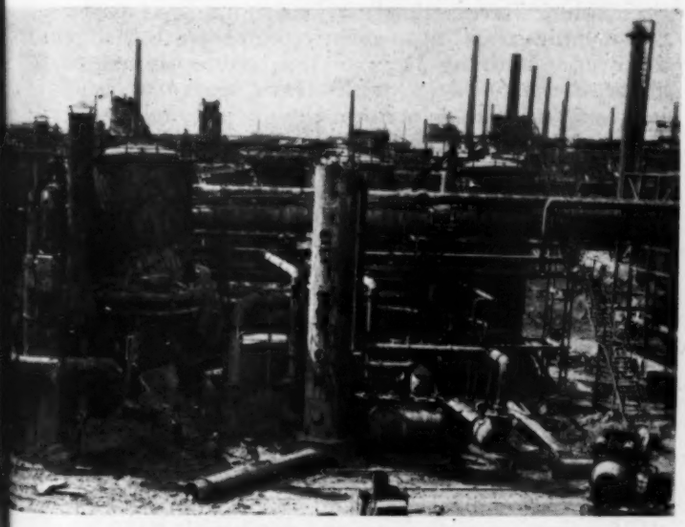
General view toward water gas machines of Ruhrchemie.



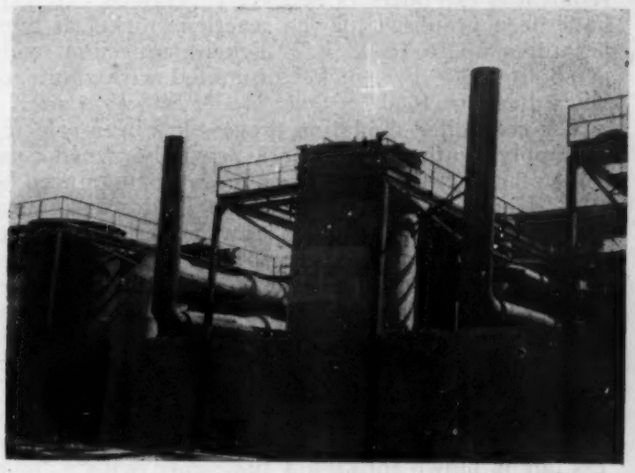
Pintsch-Hildebrand gas washer, with holders in front. Ruhrchemie unit.



Water gas plant for synthesis gas production, Hoesch-Benzin.



Hoesch-Benzin fine purification plant for synthesis gas.



Ruhrchemie fine purification plant.
Below: Sulfur-removal towers. Sulfur content of the synthesis gas must be carefully controlled and maintained at a low figure.

Top of rough and fine purification units, Kamen Dortmund.

steam reaction. In this connection, Natta and Pontelli[103] have studied the production of gas mixtures from methane plus steam and oxygen and from methane plus carbon dioxide and oxygen, the oxygen addition being desirable to supply heat of reaction by combustion of part of the charge, as well as for producing the desired gases. These investigators determined the ratio of carbon monoxide to hydrogen as a function of the initial composition of the reactant and the temperature of the reaction for the two ternary systems and for the quaternary system $CH_4 + CO_2 + H_2O + O_2$. Their experiments were carried out in a temperature range of 1470-2550° F. Brassert[173] has patented a process for the production of carbon monoxide from natural gas and gases rich in carbon dioxide, such as blast-furnace or producer gases. Other references pertaining to this reaction are [29, 65, 68, 106, 108, 111,157].

Controlled Oxidation

Since it is exothermic and thus does not require expenditures for external heating, the controlled oxidation of natural gas would seem to be more economic than the other processes, provided sufficiently-inexpensive oxygen can be obtained. Fischer and Pichler,[48] using two parts of methane to one of oxygen, a temperature of about 2550° F., and a contact time of about 0.01 second, obtained a gas containing about 54 percent hydrogen, 26 percent carbon monoxide, 9.4 percent acetylene, 4.8 percent methane, and 3.0 percent carbon dioxide. After removal of acetylene (a valuable product for organic syntheses), this gas would be suitable for use in the standard Synthine reaction without any treatment other than sulfur removal if the latter is necessary. Various catalysts have been proposed for the reaction: nickel at temperatures up to 1830° F.[97], nickel-magnesium oxide at about 1550° F.[58], nickel promoted with thoria or silica at about 1650°[82, 112, 156] etc.[29,106,108,111]

The controlled oxidation process has been selected to supply synthesis gas for a privately-owned Synthine plant, according to plans recently announced by P. C. Keith and his associates in Hydrocarbon Research, Inc.[16,113] Estimated raw materials requirements have been given as 65,000,000 cubic feet of natural gas and 40,000,000 cubic feet of oxygen per day, and it has been said that use of heat from the exothermic synthesis reaction to supply steam to power the compressors will result in a net cost for oxygen of only 5 cents per thousand cubic feet.

A new method of separating oxygen from the air has recently been publicly announced.[22] In this process, air is blown through a tube lined with a cobalt chelate compound which absorbs oxygen. When the absorption reaches its maximum, the air flow is discontinued and the tube heated to drive off the absorbed oxygen. This process is said to have been used to supply oxygen for welding and other operations in the South Pacific where regular base supplies were not available. Whether the method will prove to have industrial advantages over present large-scale processes for oxygen manufacture remains to be determined; but, if it should turn out to offer an inexpensive source of oxygen, it could vitally affect the economics of a number of chemical processes—among them, the Synthine process.

Synthesis Gas Purification

Regardless of its source, synthesis gas must be almost completely free of sulfur and its compounds for use in presently-known processes, about 1 grain per 1000 cubic feet being the maximum tolerable amount.[132] The Robinson-Bindley process of Synthetic Oils, Ltd., is said to employ a sulfur-resistant catalyst which does not require extensive purification of the synthesis gas[73]; but, in general, rigid specifications as to sulfur content have been prescribed.[14, 25, 29, 45, 47, 52, 53, 56, 73, 147] If the synthesis gas is to be produced from natural gas, future practice may involve desulfurization of the natural gas prior to its conversion. The Girbitol process,[24, 35] for example, might well be used, or any of several other desulfurization processes.

The removal of sulfur compounds from synthesis gas is usually accomplished in two steps: (1) removal of the hydrogen sulfide, and (2) removal of the organic sulfur compounds. In the German commercial plants, the removal of hydrogen sulfide was almost universally accomplished by the well-known iron oxide process.[26, 27, 66] However, at least one plant, that at Luetzkendorf, used the "Alkazid" process[99] in which an alkaline organic compound absorbs the hydrogen sulfide and then is steam-stripped for reuse.[26,123] In all the German plants examined, the organic sulfur compounds were removed by a process which consisted essentially of catalytic oxidation. The gases were passed over a Fe_2O_3-Na_2CO_3 catalyst at temperatures ranging from about 350° F. with fresh catalyst to 535° F. with nearly-exhausted catalyst. Fresh catalyst analyzed 34.4 percent Fe_2O_3 and 23.8 percent Na_2CO_3, while fully-spent catalyst contained about 33 percent Na_2SO_4, 0.3 per cent Na_2SO_3, and 4 percent Na_2CO_3. A small percentage of oxygen in the entering synthesis gas was said to be necessary for removal of the organic sulfur by this process.[26]

The hydrogen sulfide removal process in use at the Steinkohlen-Bergwerk plant was found to consist of passing the gas at atmospheric temperature through a tower containing beds of iron oxide (luxmasse) about 12 inches deep on 18 trays spaced about 40 inches apart. The velocity of the gas through the catalyst was said to be about 3.3 feet per second. According to interrogated Germans, the catalyst life was about 12 weeks, after which it was discarded. Air was added to the synthesis gas prior to hydrogen sulfide removal to function as an oxidizing agent in the subsequent removal of the organic sulfur, which was accomplished in the manner previously described. The total sulfur content of the synthesis gas after purification was said to be about 2 grains per 1000 cubic feet,[27] being somewhat higher than generally considered permissible. The effect of oxygen addition to the synthesis gas (prior to purification) on the removal of both hydrogen sulfide and the organic sulfur is particularly interesting. Hydrogen sulfide removal was said to be poor with only 0.012 volume percent oxygen; good with 0.177-0.205 percent, permitting high throughput rates; and seriously decreased when the oxygen content was as much as 0.802-0.903 percent. The removal of organic sulfur was not satisfactory with oxygen contents as low as 0.012 volume percent, but was so with 0.177-0.443 percent. Optimum overall results were reportedly attained with 0.177 to 0.205 volume percent of oxygen in the gas.[27]

A number of other processes have been proposed for the purification of synthesis gas. In one multistage process, hydrogen sulfide is removed in the first stage by moist iron oxide; a part of the organic compounds are decomposed in the second stage by the action of a mixture of sulfurized iron and an alkali metal carbonate at 570-840° F., the hydrogen sul-

fide being removed by moist iron oxide; and, in the last stage, the partially-desulfurized gas is passed over a mixture of iron oxide and alkali metal carbonate at a temperature of 300-570° F.[119, 169, 174]

The ferric oxide method for removing hydrogen sulfide is well known and long established. A plant employing a mixture of ferric oxide and wood shavings (to give permeability to the mass) has recently been described.[101] Permeability may also be obtained by molding the catalyst into small balls.[10] The equipment and detailed advantages and disadvantages of the process have been discussed by Turner.[145] The process is said to operate most effectively if the quantity of the gas is small or the hydrogen sulfide content is low. Two good bibliographies on ferric oxide purification of gases have been published recently. The first[57] includes a discussion of test procedures and experimental results, while the second[128] is well annotated.

Where the hydrogen sulfide content of the unpurified gas is high, it might prove advisable to remove the major portion by one process, then the remainder by a method (such as that using iron oxide) which gives high removal when the initial content is low. One method for rough removal might utilize the ammonia-Thylox process, which is said to reduce hydrogen sulfide in coke-oven gas from 2500 grains per 1000 cubic feet to less than 80 grains per 1000 cubic feet.[15]

Japanese investigators have done considerable experimental work on iron oxide for complete desulfurization of synthesis gas. Iron oxide was found to be effective at about 660° F. and a space velocity of 330 volumes of gas per volume of catalyst per hour.[142] They also studied the influence of various promoters for the iron oxide catalysts, finding that the addition of 10 percent each of sodium hydroxide and thoria greatly improved the efficiency of the catalyst. At about 660° F., a 7-to-3 mixture of technical iron oxide (luxmasse) and diatomaceous earth with 30 percent of sodium hydroxide was reported to reduce the sulfur to about 0.35 grain per 1000 cubic feet.[55] The addition of 10 percent of copper or nickel hydroxides and 10 percent of sodium hydroxide to luxmasse resulted in a catalyst which, at 390-480° F. and a space velocity of 250 volumes per volume per hour, was said to reduce the sulfur content of synthesis gas to less than 1 grain per 1000 cubic feet.[54]

Removal of both hydrogen sulfide and organic sulfur by reaction over iron-oxide catalysts has been claimed by several others.[164, 171, 177, 178] In one of these processes,[177] treatment with active carbon at room temperature prior to passage over the iron oxide is said to remove most of the organic sulfur compounds.

As already mentioned, catalytic oxidation may be employed for removal of the organic sulfur compounds in synthesis gas. In one experiment in which about 0.6 percent of oxygen was mixed with the gas and the mixture was passed over a catalyst of nickel hydroxide on china clay, the product (after removal of sulfur dioxide and hydrogen sulfide) contained about 10 grains of organic sulfur per 1000 cubic feet.[60]

Underwood[147] has mentioned a "specially prepared nickel catalyst" suitable for the oxidation of organic sulfur compounds to sulfur dioxide, but has not given any details on its use or the results obtained.

Organic sulfur compounds may be subjected to catalytic reduction to hydrogen sulfide, the latter being removed by iron oxide in the usual manner. Processes of this nature are said to permit much higher space velocities than processes using activated iron oxide-alkali catalysts.[132] A pumice-supported catalyst containing uranium and cerium in the ratio of 4 to 1 by weight has been used at a temperature of about 660° F. and a space velocity of 5700 volumes per volume per hour. This process was found to be less effective in removing thiophene than it was in removing carbon disulfide; and it was also observed that the presence of carbon monoxide in the gas desulfurized reduced the extent of sulfur removal as compared with the desulfurization of pure hydrogen.[2, 75]

Fischer and Tropsch have patented a number of processes for the removal of organic sulfur from water gas, several of them employing catalytic reduction to hydrogen sulfide.[159, 160, 165, 168] Catalysts for the reduction included metals such as lead, tin and copper mixed with inorganic bases or acid anhydrides, lead chromate, calcium plumbate, cupric oxide, or lead acetate[159]; and precious-metal catalysts, such as silver and gold.[160, 168] Fischer has also patented a process[161, 172] by which the hydrogen sulfide may be removed from the gas after reduction by reaction with an alkaline solution of $K_3Fe(CN)_6$.

A process for decomposing organic sulfur compounds to hydrogen sulfide by passing the gas at a temperature above 570° F. over a mixture of alkali-metal carbonates and iron oxide has been patented by Studien- und Verwertungs-G.m.b.H.[164, 169]

The I. G. Farbenindustrie A.G. has laid claim to a process for decomposing the organic sulfur compounds to hydrogen sulfide simultaneous with the water-gas-shift reaction, the reaction with steam accomplishing both purposes.[170]

Numerous reviews have recently appeared which include information on the types of sulfur compounds found in gases, their type reactions, determination, and removal.[9, 12, 51, 74, 84, 85, 98, 99, 100, 133, 150] The information on organic sulfur removal published in the period 1930-1942 has been summarized,[71] and modern gas-purification plants have been described in some detail.[99] Research is in progress at the Institute of Gas Technology,[90] and elsewhere, on the development of sulfur-resistant catalysts.

* * *

Subsequent articles in this series, as previously mentioned, will discuss the Synthine process from the standpoint of the catalytic synthesis reactions involved; the products, by-products, and derivatives obtained; and the basic economics and current developments in the field.

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Present-Day Hydrogen Manufacturing Processes

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THE production of hydrogen for various industrial purposes has increased rapidly in recent years. Relatively large quantities of hydrogen are used in the synthesis of ammonia, and in the processing of hydrocarbons of such products as aviation gasoline and lubricants, while substantial quantities are utilized in the hydrogenation of fats and oils for the manufacture of such products as shortenings and soaps. The utilization of hydrogen in the manufacture of organic chemicals is increasing rapidly, typical examples being the synthesis of methanol, the production of glycols from aldols, alcohols from esters and glycerides, amines from nitriles, and cycloparaffins from aromatics. Hydrogen is also being utilized commercially for the production of anhydrous hydrogen chloride by direct combustion with chlorine, and is being used in increasing amounts, either alone or in admixture with nitrogen, in the production of special furnace atmospheres for the heat treatment of metals and alloys. Further outlets for hydrogen in the metallurgical industry are its utilization in powder metallurgy, in the reduction of iron oxide to form sponge iron, in the processing of tungsten and molybdenum, and in atomic hydrogen welding.

Current production figures for hydrogen manufacturing in the United States[3] show a production in May, 1945, of 2.2 billion cubic feet of hydrogen (of which 1.8 billion cubic feet were consumed in the plants where it was produced), together with 3.2 billion cubic feet of hydrogen that were produced and consumed in the manufacture of synthetic ammonia, and 1.0 billion cubic feet of hydrogen that were produced and consumed in the manufacture of synthetic methanol. Similar production figures were reported for April and June, 1945.

Prior to World War II, the synthetic ammonia industry in the United States had a hydrogen production capacity of about 3 billion cubic feet per month.[5] Wartime facilities increased this capacity to about 9 billion cubic feet per month.[4] Six of the ten new wartime synthetic ammonia plants employed natural gas for the production of hydrogen, with the remaining four plants utilizing coke. Before the war, only two synthetic ammonia plants in the United States had utilized natural gas for manufacturing hydrogen.

Numerous processes have been developed for the production of hydrogen, and in addition, hydrogen has been obtained as a byproduct in the operation of a number of processes.

The following hydrogen manufacturing processes will be described below:

1. The electrolysis of water.
2. The steam-iron process.
3. The steam-water gas process.
4. The steam-hydrocarbon process.
5. The steam-methanol process.
6. The thermal decomposition of hydrocarbons.

THIS paper describes the hydrogen manufacturing processes that are in use on a commercial scale at the present time in this country. These processes include the following:

1. The electrolysis of water.
2. The steam-iron process.
3. The steam-water gas process.
4. The steam-hydrocarbon process.
5. The steam-methanol process.
6. The thermal decomposition of hydrocarbons.

The present production of hydrogen in the United States amounts to about six billion cubic feet per month, of which about three billion cubic feet per month are produced and utilized in the manufacture of synthetic ammonia.

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The Electrolysis of Water

The commercial production of hydrogen and oxygen by the electrolysis of water has been practiced for many years. When an electrical current is passed through water, hydrogen ions ($H+$) migrate to the negative electrole (cathode) where they combine with electrons to form hydrogen atoms, which then unite to produce hydrogen molecules (H_2) that escape from the water as bubbles of hydrogen gas. At the same time, hydroxyl ions ($OH—$) migrate to the positive electrode (anode), where they lose electrons and combine to produce water molecules and oxygen atoms, these combining to produce oxygen molecules (O_2) that also escape from the water as bubbles.

Because of the low electrical conductivity of pure water, solutions of potassium or sodium hydroxide in distilled water are commonly employed for hydrogen and oxygen production by electrolysis. On electrolyzing these solutions, the metal ions migrate to the cathode, where they form atoms which react with water to produce hydrogen and regenerate the metallic hydroxide. This causes a concentration of caustic at the cathode, and a dilution at the anode. To overcome this effect, the solution must be circulated through the cell, or means provided for ready diffusion between electrodes.

High current efficiencies (96-100 percent) are ordinarily obtained in electrolytic units of modern design, where gas leakage is negligible and there is no appreciable bypassing of electrical current. The current efficiency is the ratio of the quantities of hydro-

gen and oxygen actually produced to the theoretical quantities liberated by unit quantity of electricity.

The theoretical voltage required to dissociate water[1] is 1.23 volts at atmospheric temperature and pressure so that with 100 percent current efficiency and the theoretical decomposition voltage, the production of 1000 SCF of hydrogen and 500 SCF of oxygen (SCF = standard cubic foot at 60° F. and 14.7 pounds per square inch absolute pressure) would require 78.8 kilowatt-hours of direct current.

The actual minimum voltage required to produce gaseous hydrogen and oxygen from a solution of potassium hydroxide or sodium hydroxide is approximately 1.7 volts.[14] The excess over 1.23 volts is termed over-voltage. Over-voltage depends upon factors such as the composition, concentration, and temperature of the electrolyte, the current density (current flow per unit area of electrodes), the composition and form of the electrodes, the distance between electrodes and the type of diaphragm used for separating the hydrogen and oxygen.

The actual operating voltage of commercial cells electrolyzing water is ordinarily in the range of 2.0 to 2.25 volts, so that at 100 percent current efficiency, the power consumption amounts to 128 to 144 KWH per 1000 SCF of hydrogen produced.

The direct current required is ordinarily produced by the rectification of alternating current by mercury arc or other types of rectifiers. Assuming a rectifier efficiency of 90 percent, the alternating current usage for producing hydrogen by the electrolysis of water in commercial cells amounts to about 140 to 160 KWH per 1000 SCF of hydrogen produced.

The conductivity of the electrolyte increases with temperature, but the evolution of excessive amounts of water vapor limits the practical operating temperature to about 170° F. For both sodium and potassium hydroxide solutions, the conductivity passes through a maximum with increasing concentration. At 170° F. this is approximately 34 weight percent for potassium hydroxide and 25 weight percent of sodium hydroxide.[1]

Ordinarily the heat liberated by the electrolysis will be sufficient to maintain the cell at the proper operating temperature, and in many cases some cooling is required.

Since no electrolyte is consumed in the process, its replacement becomes necessary only because of mechanical losses in the outlet gas streams or contamination from the distilled water used as makeup, or from carbonation due to contact with atmospheric carbon dioxide.

Two general types of cells are in use. These are the unipolar or tank type of cell, and the bipolar or filter press type. The unipolar cells are built in two forms, namely, open and closed tanks.

In a unipolar cell, large parallel rectangular electrodes are suspended in a tank of electrolyte. Alternate electrodes are connected in parallel, an odd number of electrodes ordinarily being employed to maintain the speed tank at a uniform potential on both sides. Cells are then connected in series to a source of direct current. Cathodes are commonly made of iron while anodes are usually nickel-plated iron plates. Diaphragms between the electrodes prevent the mixing of hydrogen and oxygen, and these gases pass separately to collecting chambers above the respective electrodes. The diaphragms may be of asbestos cloth, wire screen, or perforated nickel plate. Typical examples of the open-tank unipolar cells are the Burdett, Knowles, and Fauser cells.[1, 6, 14]

Closed-tank unipolar cells include Levin, Stuart, International Oxygen Company, and Consolidated Mining and Smelting Company cells.[1, 6, 14, 15]

Figure 1 shows a battery of Consolidated Mining and Smelting Company cells, in their electrolytic hydrogen plant at Trail, B. C. The mercury are rectifiers which supply the direct current for the operation of the electrolytic plant are shown in Figure 2.

These cells[15] contain 15 electrodes (7 anodes and 8 cathodes), each about 39 inches square. The electrode spacing is 1.3 inches, and the normal operating current density is 67 amperes per square foot. With a 28 percent potassium hydroxide solution at 170° F., the cell voltage is about 2.25 volts, and the current flow is 10,000 amperes. Hydrogen of a purity of 99.9 percent is obtained, while the oxygen is 99.5 percent pure. The cell tops are constructed of concrete, the tanks are mild steel, and the diaphragms are asbestos cloth. Provision is made for external cooling of the tanks with running water, and an automatic system is provided for adding distilled water to the cells. The quantity of makeup water required will be from 6.5 to 8 gallons per thousand cubic feet of hydrogen produced, dependent upon the temperature at which the hydrogen and oxygen are discharged from the system.

The bipolar, or filter-press, type of electrolytic cell has been utilized principally in Europe. It consists of a number of electrodes in series, with diaphragms between them, and with the electrodes insulated and sealed at the edges. The electrodes and diaphragms are mounted in a frame similar to that used in a filter press. Provision is made for circulating electrolyte between the electrodes, and for withdrawing hydrogen and oxygen from the top of the space between the electrodes and the diaphragms. One side of each electrode serves as a cathode, while the other side is the anode in the adjoining cell. This arrangement eliminates the need for bus bars and other electrical connections between the cells, while the close spacing of the electrodes and the high current densities employed (200 amperes per square foot) reduce the floor space required considerably below that used with tank-type cells. However, considerable difficulty has been experienced with bipolar cells in connection with insulation, diaphragms, electrolyte circulation and impurities in electrolytes. The continued successful operation of this type of cell appears to be more difficult to maintain than is the case with the unipolar cells. Examples of bipolar units are the Pechkranz, Bamag, Shriver, and Oerlikon electrolyzers.[1, 6, 14]

Current consumption and cell voltages for the bipolar electrolyzers are the same or slightly less than those for the unipolar tank-type electrolyzers.

In all of the cells mentioned above, the hydrogen and oxygen are generated at substantially atmospheric pressure (4 inches water column for the unipolar and up to 30 inches water column for the bipolar electrolyzers). Some experimental work has been done on the electrolysis of water under high pressure, but such units are not believed to be in commercial use.

The high purity of the hydrogen produced by the electrolysis of water makes the gas suitable for practically all purposes for which hydrogen is utilized. In cases where traces of oxygen cannot be tolerated, the oxygen can be removed by passing the

FIGURE 1
Electrolytic hydrogen cells at Consolidated Mining and Smelting Company of Canada, Limited, hydrogen plant, Trail, B. C.

hydrogen over catalysts at elevated temperatures.[14]

Since the principal operating cost in the production of electrolytic hydrogen is the electrical power required, the economics of producing it are closely linked with power-generation costs, together with applications for the oxygen obtained as a byproduct.

In addition to its production by the electrolysis of water, hydrogen is also obtained as a byproduct in other electrochemical processes, such as the electrolysis of aqueous solutions of sodium chloride, for the manufacture of chlorine and sodium hydroxide, and the electrolytic process for the manufacture of chlorates and perchlorates.

The Steam-Iron Process

The steam-iron process is one of the oldest commercial processes for the production of hydrogen. This process is based upon the following reactions:

(1) $Fe_3O_4 + H_2 = 3FeO + H_2O$
$\Delta H =$ 27,300 Btu per lb. mole at 1652° F.

(2) $Fe_3O_4 + CO = 3FeO + CO_2$
$\Delta H =$ 13,200 Btu per lb. mole at 1652° F.

(3) $FeO + H_2 = Fe + H_2O$
$\Delta H =$ 6,500 Btu per lb. mole at 1652° F.

(4) $FeO + CO = Fe + CO_2$
$\Delta H = -7{,}700$ Btu per lb. mole at 1652° F.

The above reactions are all reversible and are carried out at temperatures of 1400° to 1900° F. The iron oxide used is ordinarily spathic iron ore, which has been roasted to convert the iron carbonate to iron oxide. The resulting oxide is quite porous, but has sufficient mechanical strength to enable it to be

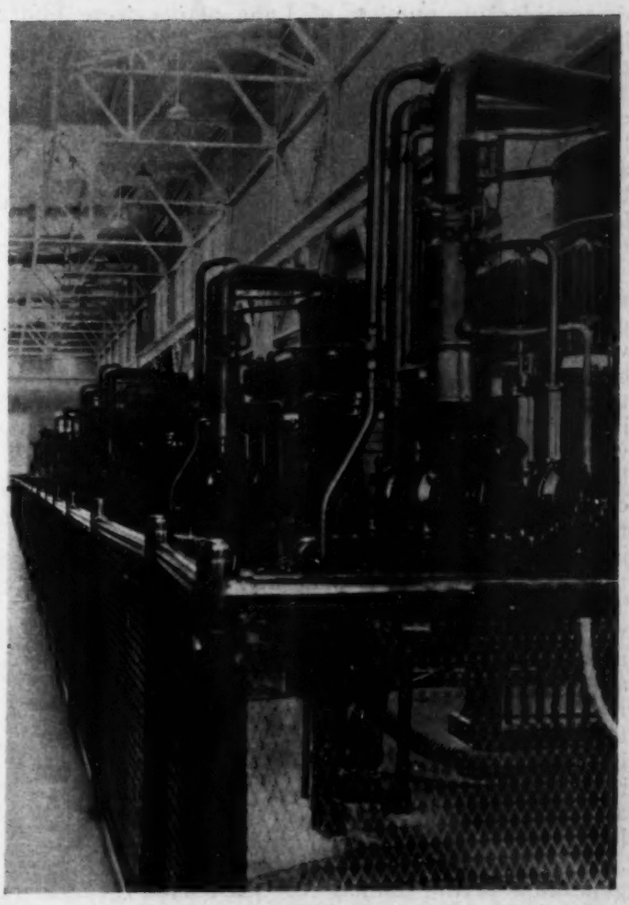

FIGURE 2
Mercury arc rectifiers for electrolytic hydrogen plant, Trail, B. C.

packed in beds 4 to 7 feet deep, using lumps ¾ to 1½ inches in diameter.

On passing a reducing gas such as water gas (containing 40 percent carbon monoxide and 50 percent hydrogen) or producer gas (25 percent carbon monoxide and 15 percent hydrogen) through the hot ore bed, the above reactions occur.

When steam is passed through the reduced oxides, reactions (1) and (3) are reversed, with the production of hydrogen and the formation of the original oxides.

Reactions (1) to (3) inclusive are endothermic, and (4) is exothermic. Since reactions (1) and (3) are reversed during the steaming cycle, the net heat change in a complete cycle due to the oxidation and reduction would be zero if a reducing gas containing only hydrogen were used. When carbon monoxide is present in the reducing gas, the net heat change in the complete cycle is that of the reaction:

(5) $CO + H_2O = CO_2 + H_2$

This reaction is exothermic, the heat liberated at 1652° F. being 14,000 Btu per pound-mol.[9]

The heat resulting from the oxidation of carbon monoxide during the reducing cycle is ordinarily not sufficient to overcome heat losses from the system so that additional heat is supplied by burning the spent reducing gas above the ore bed to heat a refractory superheater section.

The first commercial application of the steam-iron process for manufacturing hydrogen was made in 1903 by Howard Lane, an English engineer, who supplied a plant which was erected at the St. Louis Exposition in 1904 and used for generating hydrogen for inflating balloons for the Gordon-Bennett race.[8] A considerable number of Lane plants were built later for manufacturing hydrogen for the hydrogenation of fats and oils.

The Lane plant consisted of 36 vertical cast-iron retorts set in a brick furnace chamber heated by gas burners. The iron ore was contained in the retorts and reducing gas (water gas) and steam were passed through the retorts alternately by means of regulating valves. The spent reducing gas was burned in the furnace for heating the retorts.[8]

Messerschmitt[7] in 1913 invented a single retort type of steam-iron hydrogen generator that is still in general use. This consisted of a cylindrical steel vessel lined with refractory, and containing two concentric metal cylinders. The annular space between the cylinders contained the iron ore, while the inner cylinder was filled with refractory checkerwork. Heat could be supplied to the ore bed through both metal cylinders. A later design of this generator consists of a cylindrical steel shell lined with refractory and containing a single metal cylinder. The ore is charged into the annular space between the refractory lining of the outer shell and the metal cylinder. The inner cylinder is filled with refractory checkerwork. During the reduction cycle, water gas passed up through the ore bed to the top of the vessel where air is admitted to burn the spent reducing gas. The hot flue gases pass down the checkerwork and out a flue at the bottom. During the steaming cycle, steam is introduced at the bottom of the inner chamber. It is preheated on passing up through the checkerwork and then passes down through the ore bed to produce hydrogen.

A second type of single-retort steam-iron hydrogen generator is the Bamag or shaft type generator, which is also in quite widespread use. This consists of a cylindrical steel shell, lined with refractory, and

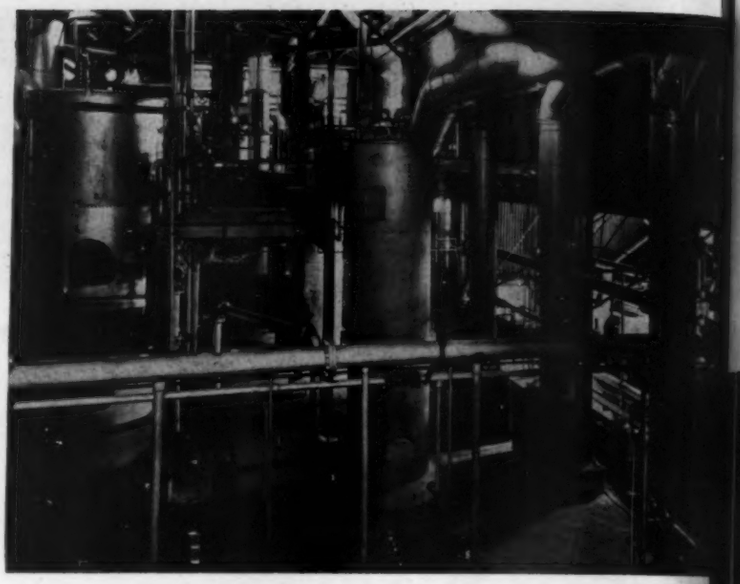

FIGURE 3

Steam-iron hydrogen plant. Generator at left, operating platform in center, hydrogen cooler at right.

containing a bed of iron ore about 6 or 7 feet deep, supported by a grate. Space is provided above the ore bed for a combustion chamber, and over this is mounted a chamber filled with refractory checkerwork which serves as a steam preheater. Openings are provided for charging and removing the iron ore. Reducing gas is admitted at the bottom of the vessel, and passes up through the ore bed. Air is introduced above the ore bed to burn the spent reducing gas. The hot flue gases pass up through the checkerwork and out a stack at the top. On the steaming cycle, steam is introduced at the top and passes down through the checkerwork preheater and the ore bed.

With both types of generators the first hydrogen produced is purged to the atmosphere to flush out reducing gas which would contaminate the hydrogen. At the end of the steaming cycle air may be passed through the ore bed momentarily to burn off accumulated sulfur compounds and carbon.

The presence of sulfur compounds in the ore bed results from their occurrence in the reducing gas. For the most part, they are converted to hydrogen sulfide during the steaming cycle and pass out in the hydrogen. Carbon formation on the ore may result from the decomposition of carbon monoxide in the reducing gas to carbon and carbon dioxide, a reaction which is catalyzed by iron oxide.[9]

Two views of a shaft type hydrogen generator and auxiliary equipment are shown in Figures 3 and 4.

A flow diagram of a plant for producing high-purity hydrogen by the steam-iron process is shown in Figure 5. The raw hydrogen from the generator is cooled and scrubbed with caustic soda solution to remove carbon dioxide and hydrogen sulfide from it. (It may contain 0.2 to 0.5 percent carbon dioxide and 0.1 to 0.5 percent hydrogen sulfide.) The hydrogen then passes to a holder. At this point it contains about 0.3 percent carbon monoxide, which is removed by mixing the hydrogen with steam, heating it to about 700° F., and passing it over a carbon monoxide oxidation catalyst (iron oxide activated by chromium) where the carbon monoxide is oxidized to carbon dioxide by the steam. The gas mixture is cooled and scrubbed with caustic to remove carbon dioxide, after which

the last traces of carbon monoxide are hydrogenated to methane by passing the hydrogen over a nickel catalyst at 500-600° F. The hydrogen is then cooled and flows to a holder for storage. The purified hydrogen produced in such a plant will contain 99.0 to 99.7 percent, depending upon the amount of purging used, with the balance being nitrogen and methane.

The materials and utilities required per thousand cubic feet of hydrogen produced by the above process are listed in Table 1.

The extent of utilization of the iron ore is very small, since one ton of ore is required for each

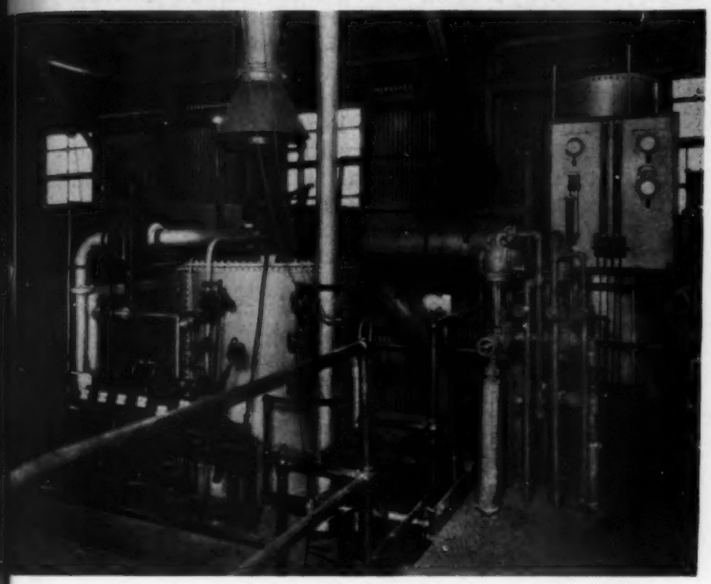

FIGURE 4
Operating platform of steam-iron hydrogen plant.

thousand cubic feet of hydrogen produced per hour, so that only about 2 percent of the ore is oxidized and reduced. The normal operating cycle is 10 to 15 minutes, approximately equally divided between reduction and steaming, with purging requiring 15 to 30 seconds, and 15 to 30 seconds being used in valve changing.[9]

The operating temperatures ordinarily employed in the ore bed are 1500° to 1800° F. The equilibria between reducing gas, steam, and iron ore are such that the degree of utilization of reducing gas increases markedly with increasing temperature, while the amount of steam required for producing hydrogen also increases with increasing temperature. Consequently the operating temperature chosen will be a compromise dependent upon the relative costs of reducing gas and steam. Above 1800° F. the life of the ore decreases noticeably, probably due to sintering. The following operating results have been reported[9] for an annular type generator operating at 1730° F.: Steam usage 155 pounds per 1000 cubic feet of hydrogen. Reducing gas usage (water gas, 90 percent carbon monoxide and hydrogen), 1480 cubic feet per 1000 cubic feet of hydrogen. Hydrogen purity, 99.0 percent. (The steam usage shown in Table 1 includes that used in water gas generation and hydrogen purification, as well as hydrogen generation.)

The iron ore used in the steam-iron generators gradually loses its activity, and must be replaced from time to time. A hydrogen production of from

TABLE 1
Process Requirements per Thousand SCF for Steam-Iron Hydrogen

Material or Utility	Quantity
Coke, lb. (for water gas production)	65 to 85 (dependent on purity of hydrogen)
Steam, lb.	500 to 600
Cooling water, gals.	1,000
Power, KWH	2.0
Ore catalyst and chemicals, cents	8.0
Fuel, B.t.u. (gas or oil)	30,000

1.5 to 3 million cubic feet per ton of ore is ordinarily obtained.

Other reducing gases, such as producer gas, may be employed for ore reduction, provided suitable provision is made for heat recovery.

While the total quantities of hydrogen manufactured by the steam-iron process are small compared

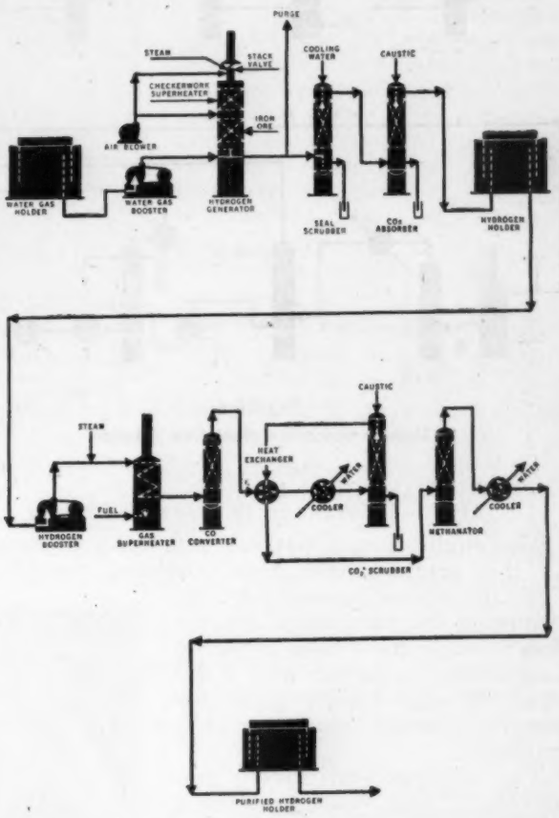

FIGURE 5
Steam-iron hydrogen plant flow diagram.

to that by such other processes as the steam-water gas or steam-hydrocarbon processes, the total number of plants that are in operation is quite large. Most of these plants have capacities in the range of 50,000 to 250,000 cubic feet of hydrogen per day.

The Steam-Water Gas Process

Water gas, which is principally a mixture of carbon monoxide (40 percent) and hydrogen (50 percent), will react catalytically with steam at elevated temperatures to produce carbon dioxide and hydrogen. Relatively pure hydrogen may then be obtained by scrubbing the carbon dioxide out of the gas mixture. This process has been utilized on a large scale for many years for manufacturing hydrogen, particularly in mixtures with nitrogen for ammonia synthesis or with carbon monoxide for the production of synthetic methanol. The reaction upon

which this process is based is the so-called water gas shift reaction:

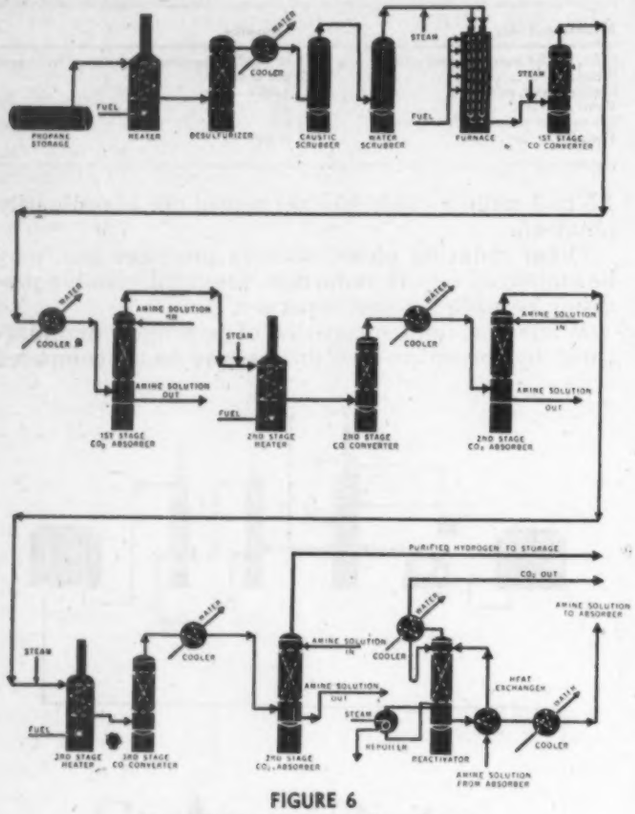

FIGURE 6
Steam-hydrocarbon plant flow diagram.

$$CO + H_2O = CO_2 + H_2$$
$$\Delta H = -16{,}500 \text{ Btu per lb. mole at } 700^\circ \text{ F. (12)}$$

The equilibrium constants and heats of reaction for this reaction have been tabulated recently.[12,16] The calculations necessary for determining the percentage conversion possible have been listed by Laupichler,[10] together with a description of a typical plant for carrying out the water gas shift reaction.

The catalyst ordinarily employed is iron oxide, activated with chromium compounds. The reaction is exothermic and although the reaction rate increases with increasing temperature, the completeness of conversion decreases at higher temperatures. Consequently, the conversion is frequently carried out in two stages, with heat exchange between them, the first stage operating at temperatures of 800-900° F., and the second at 700-750° F. By this procedure the major part of the conversion is affected with a relatively small quantity of catalyst, while the balance takes place at a lower temperature favorable to a high degree of conversion. The total quantity of catalyst required will be 400 to 600 pounds per thousand cubic feet of water gas converted per hour,[10] depending upon the operating temperature, the steam usage and the completeness of conversion desired.

With water gas containing 40 percent carbon monoxide, 50 percent hydrogen, 5 percent carbon dioxide, and 5 percent nitrogen and methane, the equilibrium composition after conversion at 750° F. with six volumes of steam per volume of carbon monoxide would be 1.2 percent carbon monoxide, 63.9 percent hydrogen, 31.3 percent carbon dioxide, and 3.6 percent nitrogen and methane, corresponding to a conversion of 96 percent of the carbon monoxide. This degree of conversion is attained in actual operation with a suitable catalyst.

In addition to the use of heat exchangers which recover all the heat necessary to maintain operating temperatures after the initial startup, a substantial saving in steam may be effected by saturating the incoming gas stream with water vapor by contacting it with hot water which has been used for cooling the outlet gas stream.

If the hydrogen produced by this method is to be used at high pressures, such as in ammonia or methanol synthesis, the carbon dioxide may be removed from the gas mixture by water scrubbing at pressures of 15 to 20 atmospheres. The residual carbon dioxide (0.6-1.5 percent) and carbon monoxide (1.5-2.0 percent) may be scrubbed out of the gas mixture at higher pressures (120 atmospheres) with ammoniacal cuprous formate solution if the gas is to be utilized for ammonia synthesis. There is a loss of 3 to 5 percent of the hydrogen in the water scrubbing operation, due to its solubility in water. This loss may be avoided, and a considerable saving in compression costs effected, by scrubbing the carbon dioxide out of the gas mixture at atmos-

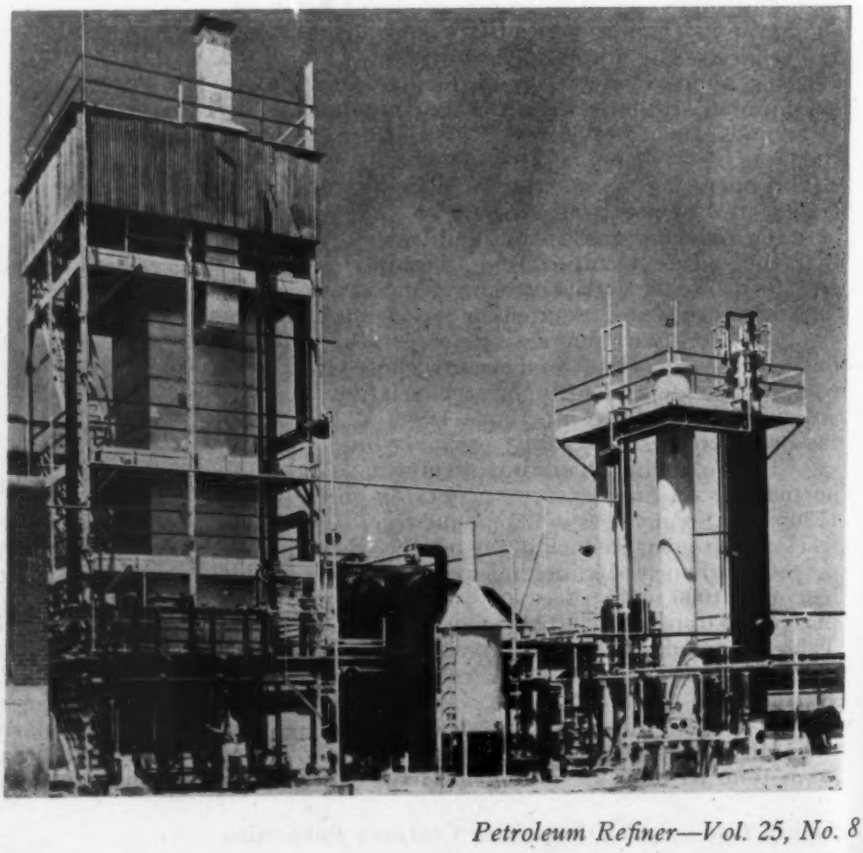

FIGURE 7
Steam-hydrocarbon hydrogen plant. Reactivator and two carbon dioxide absorbers at left, pumps, heat-exchange equipment and carbon monoxide converters in center, furnace and control house at right.

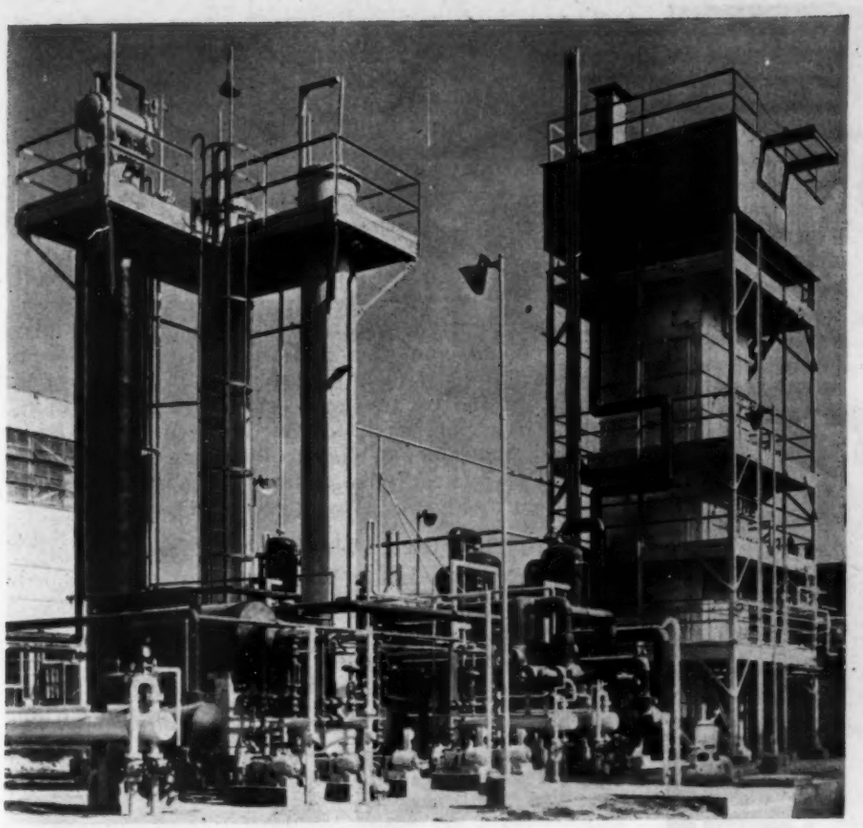

FIGURE 8
Rear view of steam-hydrocarbon hydrogen plant.

pheric pressure with amine solutions (the Girbotol Process).[12]

An analysis illustrating the composition of hydrogen which can be obtained from water gas by steam conversion followed by carbon dioxide removal at atmospheric pressure by the Girbotol Process is given in Table 2.

The quantity of nitrogen present in the hydrogen will depend upon the operating procedures used in the generation of water gas. For ammonia synthesis gas manufacture, a semi-water gas is produced, which after conversion contains the proper amount of nitrogen for ammonia synthesis.

The approximate quantities of materials and utilities required for producing one thousand cubic feet of hydrogen of the composition shown in Table 2 are listed in Table 3.

TABLE 2
Analysis of Steam-Water Gas Hydrogen

Component	Mole Percent
Hydrogen	97.2
Carbon dioxide	0.1
Carbon monoxide	1.2
Methane	0.3
Nitrogen	1.2
Total	100.0

TABLE 3
Process Requirements per Thousand SCF for Steam-Water Gas Hydrogen.

Material or Utility	Quantity
Coke, lb	42
Steam, lb	445
Cooling water, 30° F. rise, gallons	1980
Power, KWH	3.0
Catalyst and chemicals, cents	2.0

The carbon dioxide and carbon monoxide contents of this hydrogen may be reduced to any desired value by further purification, such as by the procedures outlined in the section on the steam-iron process.

It is ordinarily not necessary to remove sulfur compounds from the water gas before carbon monoxide conversion, since the catalysts used are sulfur resistant, and the hydrogen sulfide produced is removed with the carbon dioxide.

More hydrogen is produced in the United States at the present time by the steam-water gas process than by any other process, the bulk of it being utilized in ammonia or methanol synthesis. Available statistics indicate that there are approximately 10 plants utilizing this process with a total monthly capacity of about six billion cubic feet of hydrogen.

The Steam-Hydrocarbon Process

The manufacture of hydrogen by utilizing the reactions between hydrocarbons and water to produce carbon oxides and hydrogen has increased in recent years to such an extent that the steam-hydrocarbon process is now in second place with respect to hydrogen-producing capacity in the United States. At the present time, at least 17 plants with a total hydrogen manufacturing capacity of over four billion cubic feet per month use this process. Seven of these plants, with a total capacity of three billion cubic feet per month, use the hydrogen for ammonia synthesis.

The basis for the steam-hydrocarbon hydrogen manufacturing process is the fact that hydrocarbons

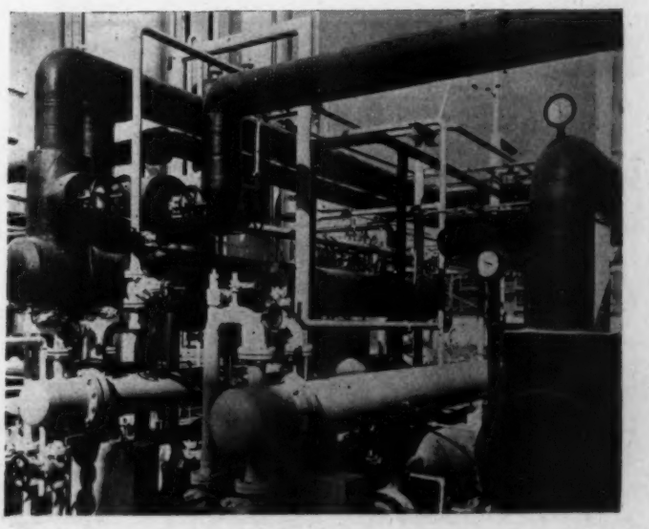

FIGURE 9
Gas heat exchangers and coolers in steam-hydrocarbon hydrogen plant.

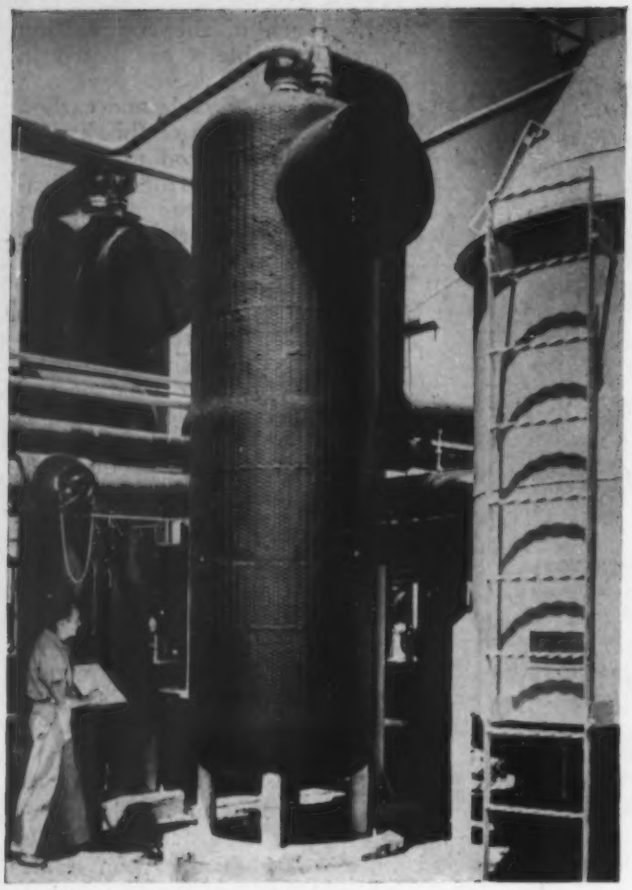

FIGURE 10
Carbon monoxide converters and standby gas heater in steam-hydrocarbon hydrogen plant.

react catalytically with steam as follows:

(6) $C_nH_{2n+2} + nH_2O = nCO + (2n + 1)H_2$

(7) $C_nH_{2n+2} + 2nH_2O = nCO_2 + (3n + 1)H_2$

Both of these reactions are endothermic. Reaction (7) is considered to be (6) followed by

(5) $CO + H_2O = CO_2 + H_2$

Similar reactions occur between unsaturated hydrocarbons and steam.

Figure 6 shows a flow plan for a plant for manufacturing high-purity hydrogen from commercial propane and steam. Propane is freed from organic sulfur compounds by being heated to 700° F. and passed over a catalyst such as bauxite, to convert the organic sulfur compounds to hydrogen sulfide, which is then removed by caustic scrubbing. The propane is then mixed with steam and passed over a nickel catalyst at temperature of about 1500° F. On the outlet of the furnace the gas mixture is cooled to about 700° F. by the addition of steam, and is then passed through the first-stage carbon monoxide converter where the greater part of the carbon monoxide is converted to carbon dioxide. The gas mixture is cooled, and carbon dioxide is removed from it by scrubbing with amine solution. The hydrogen is then purified by two more stages of carbon monoxide conversion, each followed by carbon dioxide removal. A number of views of a plant for manufacturing high-purity hydrogen from propane and steam are shown in Figures 7 to 12 inclusive.

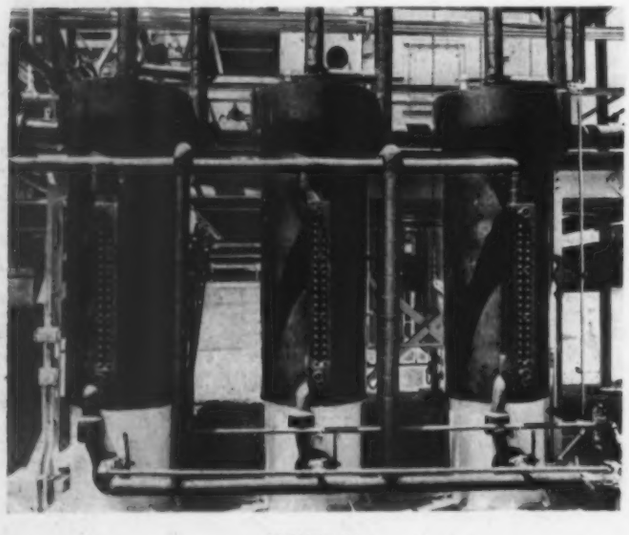

FIGURE 11
Caustic and water scrubbers in steam-hydrocarbon hydrogen plant.

The Steam-Methanol Process

Methanol and steam react catalytically to produce hydrogen and carbon dioxide at 500° F.

(8) $CH_3OH + H_2O = 3H_2 + CO_2$

A number of portable hydrogen manufacturing plants were built for the armed forces during World War II for the production of hydrogen and carbon dioxide by this process. Figure 13 shows a flow plan for this process. Methanol and water are pumped through a vaporizer where they are preheated to 500° F. and pass through a catalytic converter where methanol is converted to hydrogen and carbon dioxide. The reaction is endothermic, with heat being supplied by passing hot flue gases from the vaporizer and reboiler through the converter around the tubes containing the catalyst. The gas mixture from the converter is cooled, unreacted water and methanol are separated, and the gases are passed into the carbon dioxide absorber where the carbon dioxide is absorbed in monoethanolamine solution. The hydrogen flows from the absorbed to utilization or further purification. This hydrogen has approximately the composition shown in Table 4.

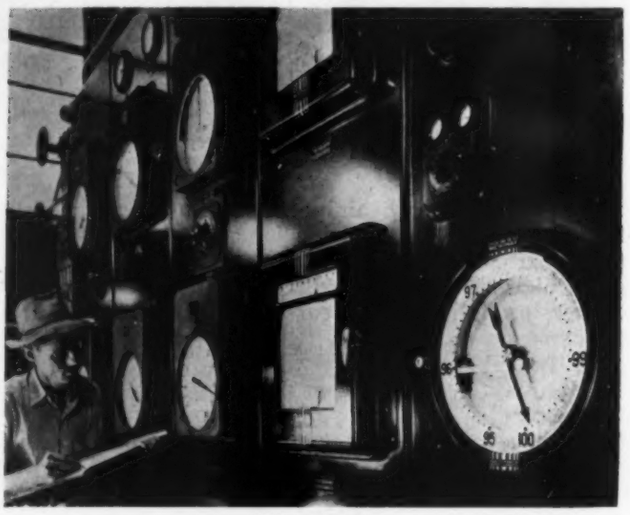

FIGURE 12
Control panel in steam-hydrocarbon hydrogen plant.

The carbon dioxide and carbon monoxide contents of this hydrogen may be reduced to any desired value by further purification.

At Low Temperature

The steam-methanol process for manufacturing hydrogen operates at temperatures sufficiently low so that the equipment may be fabricated from ordinary steel. The process may be carried out at pressures up to 20 atmospheres, so that hydrogen can be

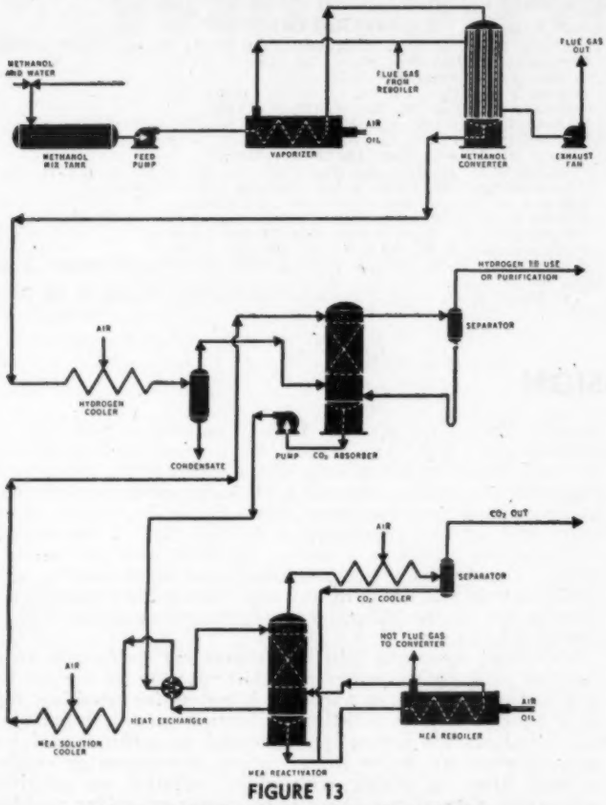

FIGURE 13

Steam-methanol hydrogen plant flow diagram.

delivered at elevated pressures if desired. Approximately five gallons of methanol and four gallons of fuel oil are required per thousand cubic feet of hydrogen produced. Thirty-nine pounds of pure carbon dioxide are produced as a byproduct with each thousand cubic feet of hydrogen.

Figures 14 and 15 show two views of a portable steam-methanol hydrogen manufacturing plant, which has a capacity of 4000 cubic feet of hydrogen and 150 pounds of liquid carbon dioxide per hour.

TABLE 4

Analysis of Steam-Methanol Hydrogen

Component	Mole Percent
Hydrogen	98.4
Carbon dioxide	0.2
Carbon monoxide	0.8
Methane	0.6
Total	100.0

The cost of methanol as a raw material precludes the widespread use of the steam-methanol process for manufacturing hydrogen, but the relative simplicity of the plant required and the ease of handling the raw materials make its use practical in certain special cases.

The Thermal Dissociation of Hydrocarbons

Methane will decompose at extremely high temperatures to give carbon black and hydrogen. This process has been utilized in one plant for producing hydrogen for ammonia synthesis.[13] Brick checkerwork is heated to 2000° F. and natural gas is then passed through until the temperature drops to 1650° F. The outlet gases, which contain about 70 percent hydrogen, are water and oil scrubbed, and the hydrogen given a final purification to remove carbon compounds by scrubbing with liquid nitrogen.

A similar process has been operated by Thermatomic Carbon Company for a number of years for the production of carbon black.[11] A brick checkerwork chamber is heated to 2550° F., after which natural gas is passed through it until the temperature drops to 1650° F. The carbon is separated from the outlet gas by bag filters. The gas contains about 85 percent hydrogen, but has been utilized only for fuel.

Summary

Six different hydrogen manufacturing processes that are employed in the United States have been described.

The largest part of the hydrogen manufactured in this country is used in the synthesis of ammonia and methanol, although the use of hydrogen for many other purposes is growing. Substantially all of the hydrogen produced in ammonia plants is manufactured by the steam-water gas and the steam-hydrocarbon processes.

The two oldest commercial hydrogen manufactur-

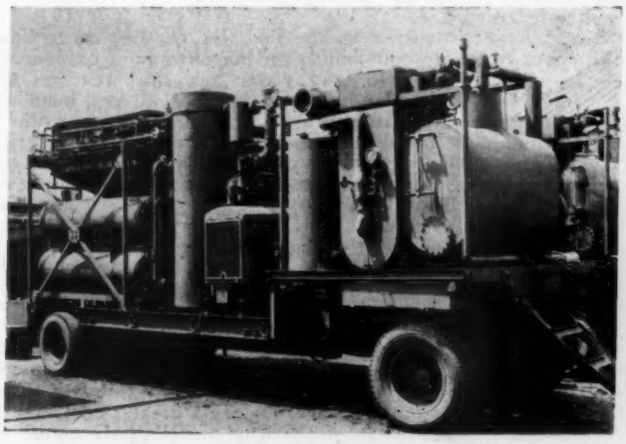

FIGURE 14

Steam-methanol hydrogen plant. From left, methanol-water storage tanks and cooler assembly, carbon dioxide absorber, gasoline engine, fuel-oil storage tank, vaporizer and reboiler, and distilled-water boiler.

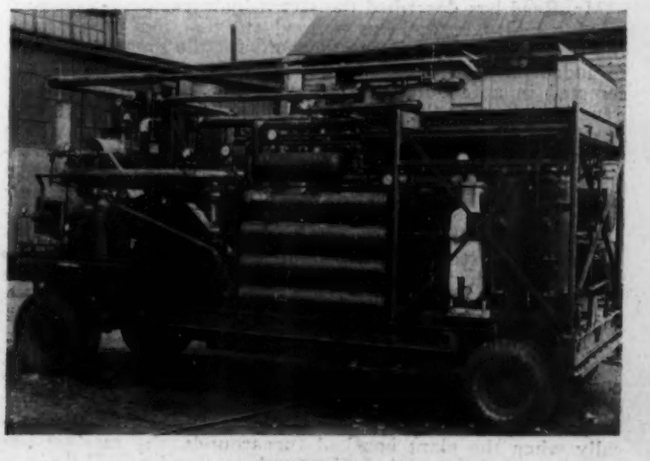

FIGURE 15

Steam-methanol hydrogen plant. From left, distilled-water boiler, vaporizer and reboiler, methanol converter, air blower, heat exchangers, cooler assembly, and carbon dioxide scrubbers.

ing processes, the electrolysis of water, and the steam-iron process, still lead in the number of plants in use, although they contribute only a small portion of the total hydrogen production, since most of these plants are relatively small in capacity.

A new hydrogen manufacturing process, utilizing the catalytic oxidation of methanol with steam, was introduced during World War II to produce hydrogen and carbon dioxide in portable units for military purposes.

The production of hydrogen by the thermal decomposition of hydrocarbons has been carried on in one plant since 1931, but no further installations utilizing this process have been reported.

The processes that have been described above account for substantially all the hydrogen manufactured in the United States, although a certain amount is recovered as a byproduct in other operations, for example in the dehydrogenation of materials such as methyl cyclohexane and butane for the production of toluene and butadiene, and in electrochemical processes.

A substantial quantity of hydrogen is obtained in Europe by the separation of hydrogen from coke-oven gas[2] but this process has not been utilized to any extent in the United States.

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DISCUSSION

R. J. Cristl *(E. I. du Pont de Nemours & Company, Wilmington, Delaware)*: Do you have any figures which would indicate the most economical plant for various capacities?

R. M. Reed: That, of course, ties in with the first cost of the plant, the capital cost. In smaller installations, of less than about two or three thousand cubic feet per hour, the electrolytic plant is the only one that has been used to any extent. Then the steam-iron process has been used in the intermediate range, and in this same range of about 5000 cubic feet per hour, the steam-hydrocarbon process is being used quite widely. These two processes are quite competitive in that range.

The initial cost of the plant for the steam-hydrocarbon process is slightly higher than that for the steam-iron process, but it has the advantage of being a continuous process, with a lower operating cost, and also it does not need the generation of water gas, which is required in the steam-iron process.

In the plant of the size of a half million cubic feet per day, or larger, the steam-hydrocarbon process is being utilized in practically all the places where natural gas is available at any kind of a reasonable cost; while the steam-water gas process will be utilized in places where natural gas or other hydrocarbons are not available or are expensive, and in cases where the presence of one percent or more of nitrogen is not found objectionable.

A. Voorhies, Jr., *(Esso Laboratories, Standard Oil Company of New Jersey, Baton Rouge, Louisiana)*: We are certainly much indebted to Mr. Reed for a very clear and interesting story on "Present Day Hydrogen Manufacturing Processes." However, I would like to make a few comments and ask a few questions.

Mr. Reed has described the steam hydrocarbon process for making hydrogen and has pointed out that this process and the steam water gas process account for the greatest amount of industrial hydrogen production. This group may be interested in a few items concerning the commercial hydrogenation plant of the Standard Oil Company of New Jersey at Baton Rouge, Louisiana, where the steam hydrocarbon process has been employed to make hydrogen since the erection of the plant in 1931. During the war years there was a considerable expansion of the Baton Rouge Hydro Plant; and the hydrogen producing facilities were accordingly increased. Up to 19 million cu. ft./day of hydrogen was produced by the steam hydrocarbon process. This corresponds to slightly under 0.6 of a billion cu. ft./month, which, for the month of May, 1945, cited by Mr. Reed, was almost 10 percent of the total U. S. production (6.4 billion cu. ft./month). In connection with this Baton Rouge plant, it is also of considerable interest to point out the ruggedness of catalyst employed for reforming methane with steam. Some of the original catalyst lumps that were placed in the reformer tubes when the plant started in 1931 are still in use. Periodically when the plant has had turnarounds, the catalyst has been removed from the tubes and screened to take out a small percentage of fines and then returned for service after the addition of some make-up catalyst.

Mr. Reed has mentioned that unsaturated hydrocarbons, as well as saturated hydrocarbons, can be employed for the steam hydrocarbon process. It may be well to point out, as doubtless Mr. Reed knows, that the process is more difficult on unsaturated hydrocarbons. With saturated hydrocarbons, particularly methane, there is no coking problem at all; and, as just mentioned, the same catalyst can be employed for years without any regeneration. In the case of unsaturated hydrocarbons, there is a coking problem, and special catalysts are employed which minimize coke formation. In spite of this we do not know of any case where the percentage of unsaturates in the reformer feed stream is more than 10 percent olefins.

Mr. Reed mentions that the chromium oxide-iron oxide catalyst used for the water gas shift reaction to convert CO and steam to hydrogen and CO_2 is not sulfur-sensitive. Perhaps he can give us a little clarification on this point since iron catalysts are normally considered as sulfur-sensitive to some degree. At Baton Rouge where the converter catalyst is used after reforming with nickel catalyst on relatively sulfur-free natural gas, there is of course no sulfur problem. The same thing is true in all of the installations of the steam-hydrocarbon-hydrogen process as employed in all the oil hydrogenation plants in this country. Since the gases going to the converter have come from passage over a nickel catalyst, there is obviously no question of sulfur contamination.

I was rather interested in the discussion of the steam-iron process, and particularly in the extent of utilization of the iron ore, which is stated to be only about 2 percent per cycle of oxidation and reduction. The problem of sintering and consequent reduction of activity seems to be the cause of the poor utilization of the ore. I would be interested in knowing of any later developments that would indicate some promise for overcoming these difficulties either by the use of different types of iron ores as such or promoted, or by the use of synthetic iron oxide.

R. M. Reed: In answer to Mr. Voorhies' question concerning the effect of sulfur compounds on the chromium oxide-iron oxide catalysts used for the water gas shift reaction to convert CO and steam to hydrogen and CO_2, several installations are in operation at present in which water gas, or other gases containing hydrogen sulfide and organic sulfur compounds, are passed over these catalysts without preliminary sulfur removal. Sulfiding of the catalyst occurs, but this does not appear to impair its activity to any extent, and as soon as equilibrium is reached, further hydrogen sulfide passes through unchanged, while organic sulfur compounds are converted to hydrogen sulfide.

A literature survey of the steam-iron process shows that numerous attemps have been made to develop a more efficient material than the conventional iron ore, but no other material has come into general use.

Reference No. 9 reports that a satisfactory artificial contact material was developed in England during World War II, but that it was not used because of its greater cost.

The low net utilization of the iron ore is partly compensated for by its relatively low cost (about $70.00 per ton), and by the fact that the large mass of ore used serves as a heat reservoir to keep the temperature changes small during the endothermic (reducing) and exothermic (steaming) parts of the operating cycle.

Furnance Tube Decoking With Steam and Air

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THE simplest and most economical method of removing coke from furnace tubes is by means of air and steam injection through the hot tubes. Many plants are utilizing this method of decoking to their distinct advantage. The savings in down time, manpower hours required and tool maintenance is tremendous and readily calculable. Many refineries have not installed the coke-burning method due to ignorance of its simplicity. Many are afraid that injury will come to their tubes and furnaces, but such is definitely not the case if even a moderate degree of control is exercised and the men performing the decoking operation are made thoroughly familiar with the process.

The method can be used on practically any type of topping or cracking-still furnace, even cracking-still furnaces with soaking tubes located in the convection banks. Naturally, extreme caution and some experience is necessary to properly decoke such a furnace without undue overheating of the roof and/or floor radiant tubes while getting sufficient heat to properly decoke the soaking tubes. The decoking of largely radiant heat furnaces is simplicity itself and no trouble of any sort should be experienced, unless the coke in the tubes contains a large proportion of salt and/or lime. The difficulty mentioned above is much more prevalent in topping furnaces, especially those which are not charged with desalted crudes.

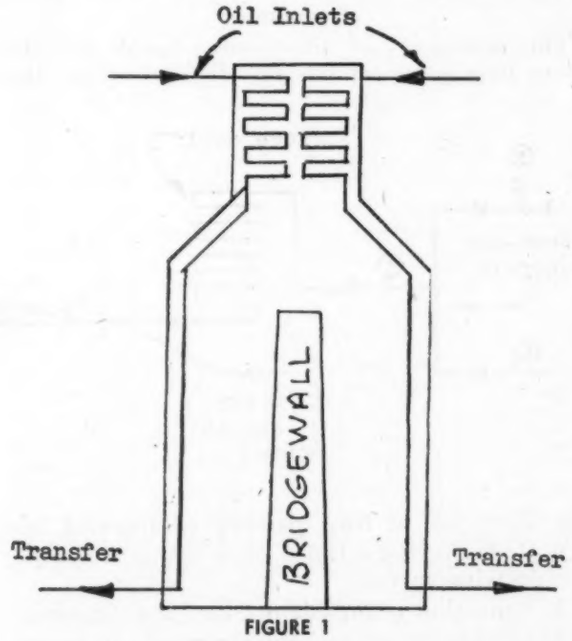

FIGURE 1

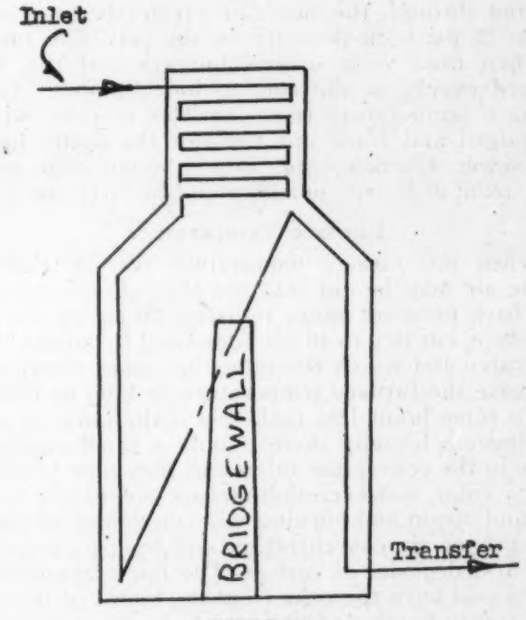

FIGURE 1-A

Many refineres are hesitant to start burning the coke from their heater tubes because no one in the organization cares to assume the responsibility of getting the program started. There is some slight risk involved if the operators are not properly schooled at the beginning, however, the writer has seen numerous cases where with only one session with an experienced burner the regular operating and maintenance crews acquired the knack of decoking and continued from then on with no interruption or deleterious results.

The Mechanics of Steam-Air Decoking

Refer to Figure 1 and 1a showing a simple upshot furnace with convection tubes in the stack outlet from the furnace. Incidentally, the furnace may be either two-coil symetrically split flow or single-coil with separate firing sides. Either type decokes with facility. A steam-air manifold is made up as shown in Figure 2 for each coil to be decoked. Several coils may be decoked simultaneously depending upon the available air supply. However, this should be no deterrent as the amount of air used in this method vs. that used in turbining is very much less and is required at a much less delivered pressure.

The outlets of the coils being decoked should be piped off to a sewer or ditch away from the unit. Considerable flake coke, dust and steam are dis-

charged from the coils with the unreacted air and create quite a mess unless properly disposed of. A water quench line should be installed in the outlet line immediately at the furnace to reduce the temperature of the effluent gases and to carry away the solids discharged from the coil. A complete schematic hook-up diagram is depicted in Figure 3. Decoking may be started as soon as the oil has been dropped and steamed from the tubes. Blinds are inserted in the inlets and outlets of the coils or spools

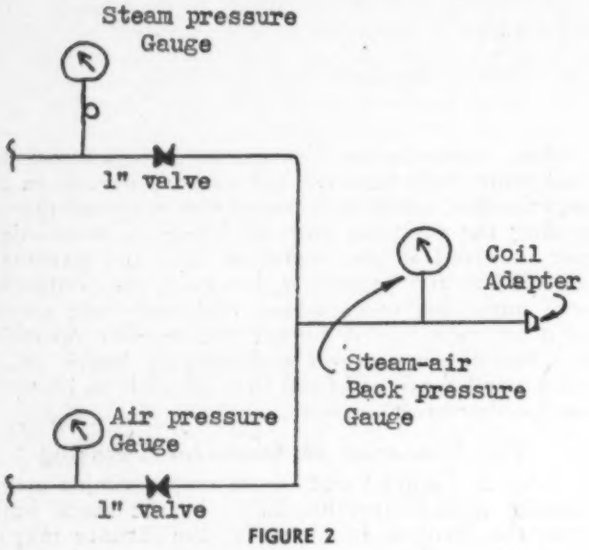

FIGURE 2

are dropped to isolate the coils for burning. Connections are made as specified above and steam is started through the tubes at a rate that will show 10 to 15 psi back pressure on the coil. The furnace is then fired with several burners and the flame spaced evenly in the combustion chamber. As the furnace temperature rises particles of coke will be dislodged and come out through the outlet line to the sewer. Quench water should be cut in to reduce the steam discharge nuisance and to carry the solids.

Furnace Temperature

When the *furnace* temperature reaches 1000° F. some air may be cut into the inlet. For instance, if the back pressure gauge registers 20 psi at this temperature, cut in 5 to 10 psi additional by means of the air valve and watch the tubes for color. Continue to increase the furnace temperature to 1100 to 1150° F. or to some point less than this if the burning starts as desired. Usually there is only a small amount of coke in the convection tubes and they may not attain much color, however they act as preheaters for the air and steam and burning will commence as soon as the proper air concentration and temperature reach the first deposits of carbon. The hot gases from the tubes will burn the coke from the inside of the headers, return bends and fittings. As burning progresses the tubes should be very closely watched by the operators and/or inspectors and not be allowed to attain more than a medium cherry red heat. Due consideration must be given the tube composition when the tubes are allowed to cool after burning. Alloy tubes and headers should be cooled with the header doors closed to prevent shock cooling and subsequent hardening. However, the danger from this source has been grossly over-exaggerated by some refinery operators. For one's own satisfaction it might be well to check with the tube manufacturers. The writer is familiar with several furnaces containing alloy tubes and headers which have shown no appreciable change in over five years of steam-air decoking. It might be well to mention here that tube color is much more pronounced at night and for that reason some operators prefer to conduct their burning during the night hours. This item assumes special significance for beginners in the art.

Watch Color

Should burning cease at any time, when there is still coke in the tubes, the air should be increased until burning resumes at which time the tubes should be closely watched for excessive color. To discontinue burning at any time it is only necessary to cloes the air valve. The air should be maintained at a point which produces an even burning rate and the furnace temperature maintained constant. The tubes should be burned at the minimum furnace temperature possible that will give a satisfactory rate of burning and finally clean tubes. After the coke has burned from the tubes they will lose their color and remain dark until all are decoked unless the furnace temperature is high enough to impart color to them. This latter condition should be avoided if at all possible.

After the tubes are clean and the furnace fires cut, they should be steamed until, in the operators' opinion they are cool enough. Some operators inject water into the cool tubes to remove residual material remaining from the burning operation. The writer does not recommend the water injection except in cases where there may be sodium and calcium chloride deposits.

Economics

The economies of the system speak for themselves once a refiner has installed steam-air decoking. They are at least partialy enumerated below.

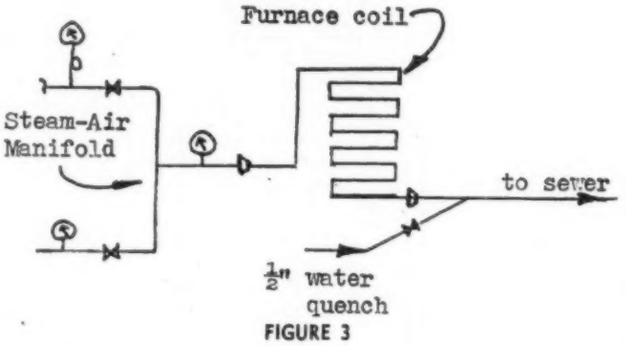

FIGURE 3

1. Reduced down time, when furnace cleaning is the delaying factor.
2. Reduction in man hours for tube cleaning.
3. Elimination of tool miantenance and repair.
4. Increased tube life.
5. Increased ease of tube and header inspection.
6. Elimination of tube turbining mess and noise.

Steam-air decoking has been successfuly used, to the writer's knowledge, on the following furnaces: Alcorn, Upshot, Equiflux, Lummus, Winkler-Koch, Kellogg, Smith, Donnelly and Foster-Wheeler. Each type requires a slightly different technique but all have been successfully decoked to the refiners' complete satisfaction.

Selection and Application of Break-Inducing Reagents in Doctor Treating

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ALTHOUGH all processes for sweetening hydrocarbon distillates involve heterogeneous reactions, and, in many cases, reactions between immiscible liquids, it is only within the last few years that the effects of interfacially surface-active materials on the course of such reactions have been examined. It is now known that the use of small amounts of specific surface-active compounds may greatly affect the practical results obtained in doctor treating, caustic washing, "Solutizer" sweetening and other processes involving contact of liquid hydrocarbon with an immiscible liquid phase.

It is the purpose of the present paper to discuss, in particular, the application of specific organocolloids in doctor treating and to outline the methods used in selecting the most effective reagents.

It has been found that the introduction of certain surface-active compounds into the distillate or into the doctor solution prior to or during the doctor-sweetening operation leads to a quicker "break" with faster and more complete wetting and subsidence of precipitated lead sulfide or other lead compound.[1] In addition, less elementary sulfur is required for completion of the sweetening reactions, and the amount of interfacial emulsion obtained on settling is considerably lessened or eliminated. Further, the amount of foaming encountered during the regeneration step is greatly reduced. The reduction in the amount of elementary sulfur required for sweetening is believed to be an important feature of the process, since evidence indicates that excess elementary sulfur, which is usually required in the doctor-sweetening operation, is responsible for certain undesirable characteristics in the finished distillate, such as poor tetraethyl lead susceptibility, poor inhibitor susceptibility, and increased gum-forming tendencies.[2]

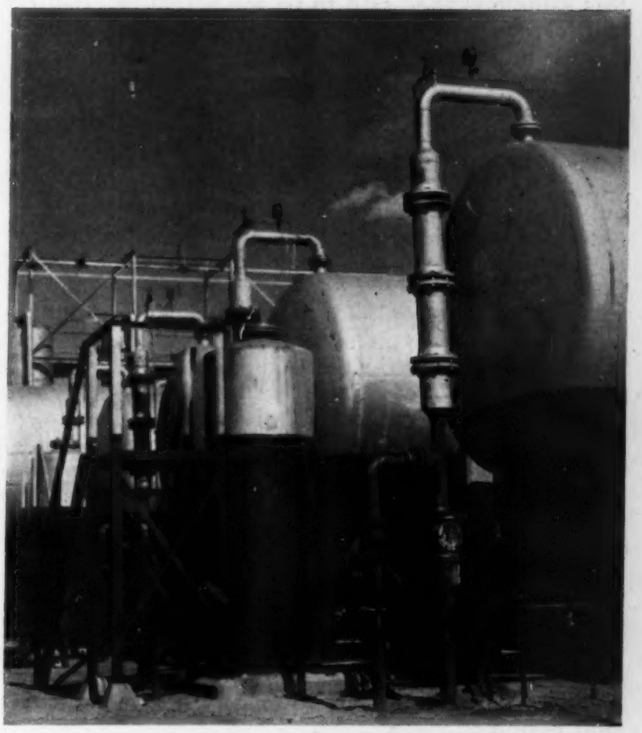
It has been found by experience that the action of the break-inducing reagent is somewhat specific; i.e., certain gasolines and certain doctor solutions require particular reagents which may be different from those required by other gasolines and doctor solutions. Because of this specificity of action, it is important that the reagent to be used be selected with care.

Testing Procedure

Before tests are made to determine the proper break-inducing reagents required, a determination of the actual sulfur requirement for sweetening without a break-inducing reagent is made. The procedure used is as follows:

One hundred ml. of gasoline are placed in a 6-ounce bottle. 10 ml. regenerated doctor solution are then added, and finally the calculated theoretical amount of elementary sulfur required for sweetening[3] is added in the form of a toluene solution of rhombic sulfur. Sample bottles containing gasoline, doctor solution, and sulfur are prepared in which the amount of sulfur added is varied from slightly below theoretical to from 100 percent to 200 percent more than theoretical. The air is then swept out of these bottles with a current of natural gas, after which they are stoppered and shaken in a shaking machine at the rate of 150 strokes per minute for one minute. The bottles are then removed from the machine and allowed to stand for a minute or two while observations are made as to which samples have broken. The break may be recognized by a rapid sedimentation of suspended matter leaving a clear, water-white distillate layer. Just preceding the break the gasoline may have a green to deep orange or red color. If none of the samples have broken after the one minute shaking period, they are again placed in the machine and shaken for another minute.

After this total two minutes of shaking, the sample showing a break which contains the least amount of sulfur is noted. The amount of sulfur contained in



Contact piping in doctor plant

TABLE 1

Break-Inducer Used	Ratio of Distillate to Break-Inducer	Actual mg. Sulfur Used per 100 ml.	Character of Break	Doctor Test on Distillate	Butyl Mercaptan Test on Distillate
None	....	6.0	None	.....	.....
None	....	7.0	None	.....	.....
None	....	8.0	Good	Negative	Positive
Sodium Stearate	5,000	6.0	None	.....	.....
Sodium Stearate	5,000	7.0	Fair	Negative	Positive
Sodium Oleate	5,000	6.0	None	.....	.....
Sodium Oleate	5,000	7.0	Fair	Negative	Positive
Sodium Abietate	5,000	6.0	None	.....	.....
Sodium Abietate	5,000	7.0	Fair	Negative	Positive
Tretolite L-6099	20,000	6.0	Good	Negative	Negative
Tretolite L-10210	20,000	6.0	Good	Negative	Negative

this sample is then said to be the actual or practical sulfur requirement for the gasoline. It may range from a few percent more than theoretical up to 200 percent, or even more than the theoretical sulfur requirement.

For the preliminary selection of the break-inducing reagent required, various samples are prepared as in the above procedure except that sulfur equivalent to only 80 percent or 90 percent of the actual sulfur requirement is added to each sample. Following the sulfur addition, various break-inducers are added to the gasoline layer in the form of 2-percent solutions in xylol or other suitable inert solvent. Such dilute solutions are used in order to permit accurate and convenient volumetric addition of the small amounts of reagent required. Usually preliminary tests are run with 1 ml. of a 2-percent solution. Air is then swept from the bottles and they are stoppered and shaken for one minute. The observations are made, and if no breaks are obtained, they are shaken for another minute or two, after which observations are again made. If one of the break-inducers used in this series of tests is at all effective, one of the samples will show a reasonably good break after this period of agitation. Sometimes it will be found that two or three reagents will give fairly good breaks. In those samples showing a break, the clarity of the gasoline and the amount and stability of any interfacial emulsion is noted.

After a series of such tests, several reagents showing some effectiveness under the conditions of the test will be found. Final tests are then made with each of these particular reagents, and varying amounts of sulfur, less than the amount originally used, are employed. By this process of elimination one or two reagents are found which will give a satisfactory break with the least amount of sulfur after two or three minutes of agitation. Often the best reagent will be found to give a satisfactory break with the theoretical or slightly less than the theoretical amount of elementary sulfur while simultaneously preventing the emulsification of doctor solution and gasoline.

In the above procedure all the break-inducing compounds are added in the form of 2-percent soutions in xylol or other inert solvent. However, it has been found that in many cases a better break is obtained or less reagent is required if the reagent is added first to the doctor solution.

For this reason a duplicate set of tests is usually run in which the surface-active agents are added directly to the doctor solution. The tests otherwise are identical with the above. In these tests in which the break-inducing agent is added to the doctor solution, the mixture of solution and break-inducing reagent is heated and shaken for several minutes to insure complete dispersion and solution of the reagent. Usually a 0.4-percent solution of break-inducer in doctor solution is prepared. For testing the reagent in more dilute form, this solution may be mixed with straight doctor solution.

For final tests on any particular gasoline, samples of the actual regenerated doctor solution to be used in the plant should be employed. Such plant doctor solutions may vary in caustic concentration from 5° Baume up to 30° Baume and may vary widely in actual lead oxide content. Also they may contain salts of acidic constituents, such as phenols and naphthenic acids which have been extracted from hydrocarbon distillates during the period of their use. For this reason no recommendation of the proper break-inducing reagent should be made without tests with the plant doctor solution.

It has been found by experience that the plant doctor solutions used on gasolines or other distillates which have previously been given an efficient caustic wash behave in general very similarly to freshly prepared doctor solution.

Results Obtained With Break Inducers

The extent to which the sulfur required for a break may be reduced by the use of small amounts of properly selected surface-active compounds is illustrated by the results shown in the following tables.

Table 1 shows the results of tests made by the above described procedure with a sample of gasoline from a Louisiana crude oil. This distillate and a theoretical sulfur requirement of 6.0 mg. per 100 ml. For comparison, three common surface-active compounds, sodium oleate, sodium stearate and sodium abietate were included. Portions of the treated gasoline were examined for the presence of mercaptan and excess sulfur by the doctor test[4] and the butyl mercaptan test,[5] respectively.

It is to be noted that a 33 percent excess of sulfur was required for a satisfactory break with this gasoline, but such treatment resulted in a positive butyl mercaptan test on the sweentened distillate. Although common soaps have been recommended in doctor sweetening,[6] it is seen that their use does not greatly improve the break. Especially selected commercial products, however, yield excellent breaks when used in small amounts. An important result of the treatment when employing the commercial products is the rapid subsidence of "lead sulfide," and the almost complete absence of interfacial emulsion.

The results obtained with an East Texas gasoline are shown in Table 2. This distillate had a theoretical sulfur requirement of 3.0 mg. of sulfur per 100 ml.

Here again, it will be noted, a large excess of sulfur

TABLE 2

Break-Inducer Used	Ratio of Distillate to Break-Inducer	Actual mg. Sulfur Used per 100 ml.	Character of Break	Doctor Test on Distillate	Butyl Mercaptan Test on Distillate
None	....	3.0	None	.....	.....
None	....	4.0	None	.....	.....
None	....	5.0	Good	Negative	Positive
Sodium Stearate	5,000	3.0	None	.....	.....
Sodium Stearate	5,000	4.0	Fair	Negative	Weak Pos.
Sodium Oleate	5,000	3.0	None	.....	.....
Sodium Oleate	5,000	4.0	Poor, Slow	Negative	Weak Pos.
Tretolite R-1	20,000	3.0	Good	Negative	Negative
Tretolite L-10210	25,000	3.0	Good	Negative	Negative

was required for a satisfactory break in the absence of a break-inducer. The addition of soaps were of some benefit but did not completely obviate the excess sulfur requirement. The commercial reagents permitted the use of a minimum amount of sulfur while eliminating the formation of an emulsion at the interface between doctor solution and gasoline.

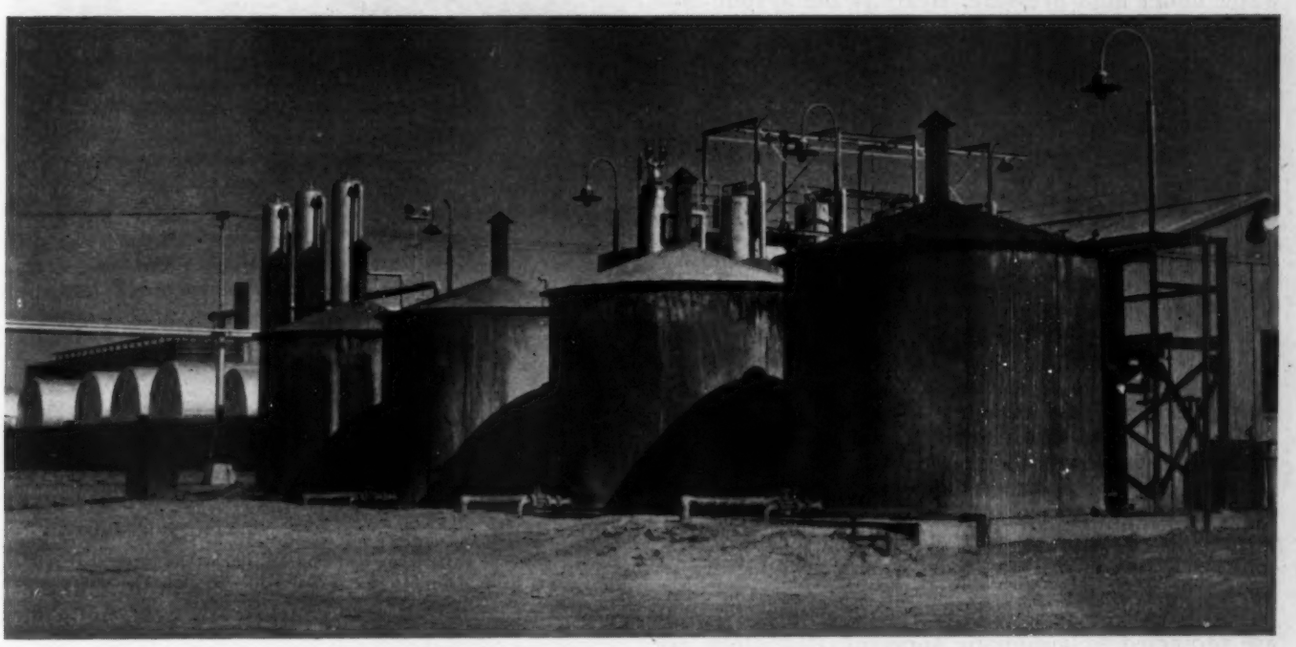
Practical Application of Break Inducers

In actual plant doctor-sweetening operations the break-inducing reagent may be added continuously either to the distillate or doctor solution, or to a mixture of the phases. The point of addition of the reagent should be such that it is present during the period of agitation of doctor solution and hydrocarbon.

In batch-treating plants it has generally been found convenient to add the required amount of break-inducing chemical to the doctor solution in the regenerator. During the regeneration stage the chemical becomes uniformly mixed in the solution and is effective during subsequent use of the doctor solution. After the initial addition of break-inducer to the doctor, small make-up amounts may be required from time to time to insure a continuous high level of effectiveness.

In continuous-treating plants, the break-inducer usually is introduced continuously into the doctor stream by means of a chemical-proportioning pump. The rate of addition is maintained at a high value until the concentration of chemical in the solution is such as to give satisfactory results. The rate of injection is then lowered to a point which will maintain the activity of the solution. In some instances, best results are obtained by continuous additions of small amounts of break-inducer to the gasoline stream before it enters the mixers.

The amount of break-inducing chemical required in actual plant practice varies somewhat since it is related to plant variables such as composition of hydrocarbon, impurities in the hydrocarbon, composition of the doctor solution, degree of agitation during mixing of phases, sedimentation time, and the like. In a typical plant, break-inducing chemical is added rapidly to the doctor solution to give a concentration of from 4 to 6 gallons of chemical per 100 barrels of doctor. The rate of chemical addition may then be reduced to 1 gallon, or less, per 100 barrels of doctor, to maintain good results. With particularly troublesome gasolines, somewhat higher initial concentrations of reagent may be required, while with many gasolines, very low concentrations of reagent will result in marked improvements in the sweetening operation. There appear to be no difficulties arising from the use of somewhat larger amounts of chemical than the minimum required for satisfactory operation. In general, the reagent requirement for a given sweetening system can readily be found by trial.



Doctor treating plant in West Texas refinery. Solution tanks in foreground

The improvements in treating plant operation usually observed when a properly selected surface-active chemical is employed include the following:

1. Quicker break,
2. Lower sulfur requirement,
3. More complete wetting and subsidence of lead compounds,
4. Less emulsification and loss of gasoline, and
5. Less foaming during regeneration of doctor solution.

The use of break inducers does not, however, lessen the desirability of good control and proper adjustment of plant variables such as degree of agitation and sedimentation time, although it often widens the limits of conditions within which proper sweetening may be obtained.

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[1] Blair and Boydstun, U. S. Patents 2,208,505 through 2,208,510 dated July 16, 1940.
[2] Lowry, Dryer, and Sutherland, Ind. and Eng. Chem. 30, 1275 (38).
[3] For method of determining the theoretical sulfur requirement for a hydrocarbon see "Laboratory Test Methods for Petroleum and Its Products," Universal Oil Products Co., Chicago, Ill., 1937 p. 206 (Method H-19).
[4] Ibid, p. 210 (Method H-41).
[5] Ibid, p. 205 (Method H-19).
[6] Sutton, U. S. Patent 2,157,223 dated May 9, 1937.

Automatic Fire System Guards Gasoline Plant

JOHN C. ALBRIGHT

FIRE protection is provided at the Los Angeles County, California, gasoline plant of Del Valle Gasoline Company by an automatic system which delivers water under high pressure. Heart of the system is a centrifugal pump driven by an electric motor which starts when an outlet from the fire-fighting water system is opened manually or through melting of fusible plugs.

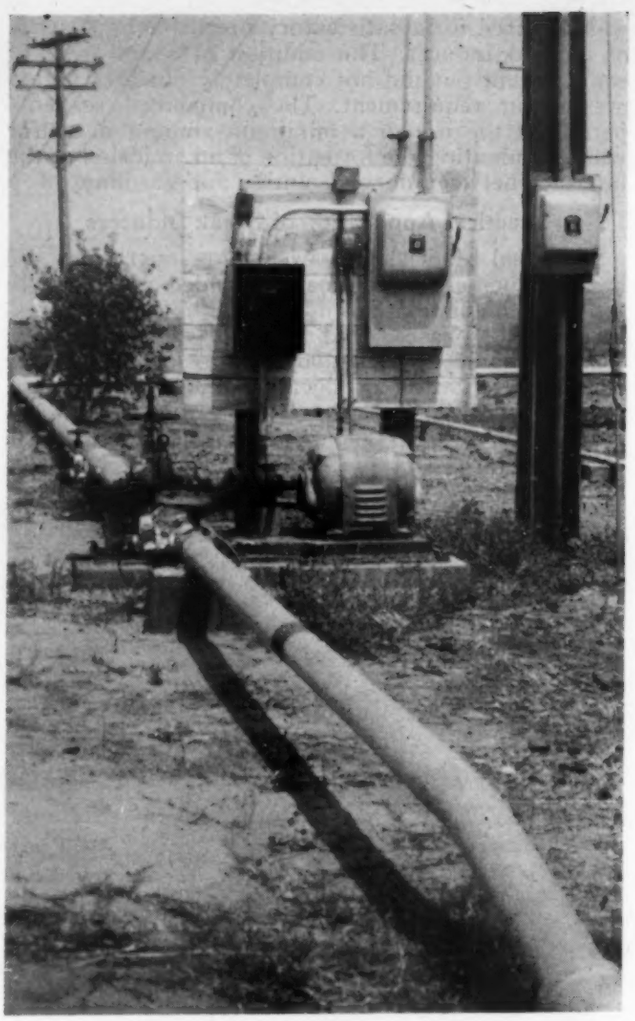
Water source for the fire system is the discharge of the cooling pumps, which is constant so long as circulation is maintained. A line connected into the pipe leading from the circulation pumps is attached to the suction of the fire pump, which is idle so long as no discharge leaves an outlet. A 40-horsepower motor is direct connected to the centrifugal pump, whose suction and discharge are 4-inch pipe. Immediately downstream from the pump is an instrument which reacts to flow of water through the system. Electric relay leads connect this instrument with the motor control which starts the motor to full power, delivering water through the system as long as an outlet is open and supply is available.

The system is laid through the main section of the plant with laterals to vital points. Hoses and nozzles are located in steel closets at other strategic points. Nozzles are the type which produce water mist.

Tanks storing gasoline or other petroleum liquids are protected by automatic spray nozzles which are brought into service by the melting of a fusible link in a chain connected to a quick-opening valve. The lever of the valve carries a weight that drops to open it.

The motor controls contain a switch to operate an alarm in the office to warn of any fire in the plant.

The system is so sensitive that if a common garden hose is attached and the nozzle opened, the motor starts and continues operating until shut off.



Electric-powered water pump and controls which start it automatically in case a fire heats a fusible link in Del Valle Gasoline Company's plant.

Below — Fog nozzles at head of propane tanks blanket the area with mist when water pressure is supplied by automatic fire pump.

Weight-operated quick-opening valves as shown here are located at danger spots throughout the plant, and valves open by action of the weight when it is released by melting of a fusible link in the supporting line. The link melts at 190° F. The fire pump starts when water flows from line.

Earnings—A Function of Catalyst Activity

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CONSIDERABLE confusion exists with regards to the terms "catalyst make-up" and "catalyst loss." "Catalyst loss" in this paper is taken to mean that quantity of catalyst which is mechanically lost from the system. "Catalyst make-up" is taken to mean the sum total of catalyst added to the system to make up mechanical losses plus catalyst added to the system (balanced by physical catalyst withdrawal from the system) to maintain optimum catalyst activity. For example, TCC units will operate on clay catalyst with a mechanical loss of 0.1 pounds per barrel. This paper shows, however, that to maintain optimum catalyst activity from the standpoint of economics, equilibrium catalyst should be withdrawn from the system and replaced with additional fresh make-up. For the example taken in this apper, the total optimum catalyst replacement is indicated to be 0.8 pounds per barrel for maximum profit.

AN ECONOMIC study is presented in this paper showing the relation between earnings and catalyst activity in a TCC catalytic cracking unit. Clay catalyst was used for the study since commercial operation for the greatest number of years has been with catalyst of this type and considerable data have been collected showing the relation between equilibruim catalyst activity and catalyst-replacement rate. Further, an accurate correlation of cracking variables, based on pilot-plant data, was available which could be used to show the effect of incremental change of clay-catalyst activity on product distribution. It is believed that the general conclusions reached will apply in a relative manner to other catalysts with the final choice of catalyst type being dictated by economics.

From the present economic study it is concluded that maximum earnings are realized from a TCC commercial plant when the clay catalyst replacement rate is in the range of 0.5 to 1.0 pounds per barrel of feed stock. This corresponds to an equilibruim catalyst activity range of 30-32 A.I.

It should be mentioned at this point that activity index is determined by a standard method designated as CAT-A which was adopted in its present form in 1944. The activity index is a measure of gasoline produced when cracking a specification light East Texas gasoil under a set of fixed operating conditions in laboratory-scale equipment of standard design. A detailed description of the method has been described in the literature by Alexander and Shimp.[1] This method is employed by all operators of Houdry and TCC catalytic cracking processes.

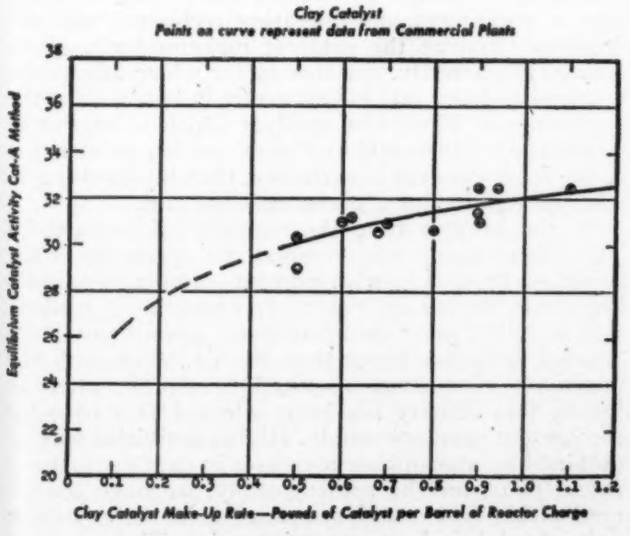

FIGURE 1
Equilibrium catalyst activity vs. catalyst make-up rate.

Factors Affecting Catalyst Activity

During normal TCC cracking operations, the equilibruim catalyst activity depends on the catalyst replacement rate and the activity of the new catalyst added. Figure 1 shows the effect of makeup rate on activity when adding new 40 A.I. clay catalyst. These results are achieved by careful control of the variables which affect catalyst life and in addition, by design features which are built into TCC plants for the specific purpose of protecting the catalyst from conditions that would cause rapid aging.

The degree of activity decline depends on the condition of time, temperature and steam partial pressure to which the catalyst is subjected during the various stages of its cycle around the unit. These factors are all interrelated. Thus, high temperatures are much more detrimental to the catalyst activity when steam partial pressures are high, and for a given temperature and steam concentration, the aging effect increases with increase in length of time at those conditions. Conversely, quite high partial pressures of steam are tolerable if the temperature is low and the time of exposure is short. Likewise, the catalyst can be subjected to relatively high temperatures, 1150-1200° F., for short periods without deleterious effect, provided steam is not present.

A knowledge of these various factors affecting

catalyst activity has played an important part in the design of the present commercial TCC unit, and each section has been reviewed in relation to its effect on the equilibruim activity to be expected.[2] Thus, the kiln has been designed to conduct the burning in separate stages, each of which is separately controlled by water-cooling coils to limit the temperatures. Having this flexibility and knowing the concentration of steam in each zone of the kiln, the temperature can be adjusted to avoid the existence of high steam concentration and high temperature in the same zone. It should be mentioned that no steam is added to the kiln other than the trace of moisture normally present in the air plus a small quantity from the air line burner. The main portion of steam that is present originates from the combustion of hydrogen in the catalyst deposit and from the desorption of water which was adsorbed by the catalyst in the reactor and oil-purge sections.

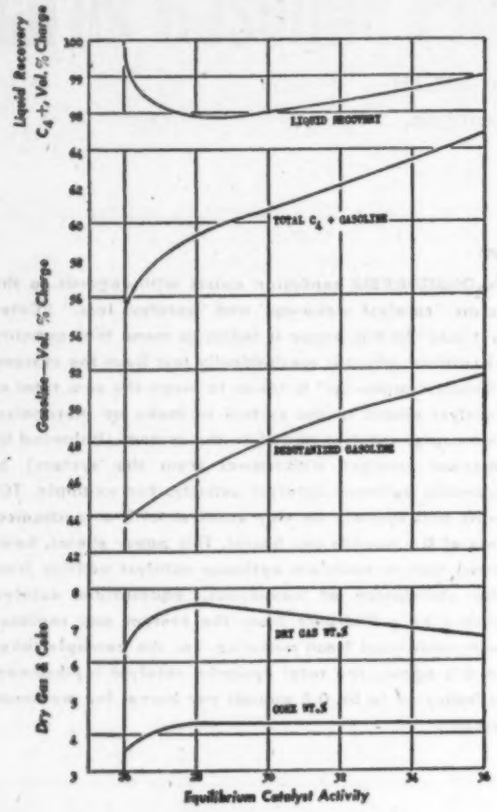

FIGURE 2
Catalyst activity vs. product distribution.

Catalyst Temperatures

When the spent catalyst enters the kiln the hydrogen and sulfur contained in the catalyst deposit burn preferentially, and at the same time the desorption of water occurs rapidly as a result of the rise in catalyst temperature. Thus, the bulk of water and SO_2 will be released in the first two or three zones of the kiln. Consequently, the catalyst temperatures are kept relatively low (875-975° F.) and the residence time is kept short. During the later stages of the regeneration and in the final cleanup zones where combustion of almost pure carbon takes place, the temperatures may be safely increased and the residence time lengthened. Relatively high temperatures of the order of 1100-1150° F. are required for the efficient and complete cleanup of the catalyst within a reasonable length of time.

Economic Study

The economic study which has been developed applies to a TCC unit which has a reactor charge capacity of 10,000 barrels per stream day and which is equipped with a kiln capable of burning 5500 pounds per hour of coke. The yield structure is based on the use of clay catalyst when single-pass cracking a heavy Mid-Continent dewaxed distillate possessing the following physical characteristics:

Gravity—°API	30.3
Distillation	Vacuum Dist. Corr. to 760 MM
IBP	496
10%	616
50%	720
90%	797
E.P.	825
Aniline No. °F.	187
Pour — °F.	15
Sulfur—Wt. %	0.24

This particular stock was used for the present study because a rather complete and reliable correlation of operating variables was available for setting up the effect of incremental changes in catalyst activity on yields. Such information is essential in order to establish optimum yields for the operations under consideration, particularly where certain conditions are arbitrarily fixed and only one or two variables are changed to show their effects. As will be noted in the yield data presented below, the chosen charge stock possesses unusually good cracking characteristics. This is indicated by the high level of gasoline yields obtained from single-pass operation. Other stocks will have different cracking characteristics and may give either higher or lower gasoline yields than the example stock, but it is reasonable to expect that the effects of catalysts activity change will be similar.

Catalyst Makeup Rates

Figure 1 is a graph showing the catalyst makeup rates required for various equilibrium catalyst activities. This curve is based on average past commercial experience for all plants utilizing clay catalyst and operating on a variety of charging stocks. It is felt that the curve is conservative when viewed from the standpoint of future operations where improved design of equipment and operating technique will undoubtedly reduce the catalyst makeup for a given equilibrium activity. Another factor which affects the required makeup rate is uniformity in hardness of the new catalyst. Thus, new catalyst which is inferior in this respect will result in a situation where attrition of the fresh catalyst is excessive, thereby resulting in a lower activity for a given makeup rate.

At the present time the majority of commercial TCC plants using clay catalyst are operating in the range of 29-31 A.I. with makeup rates approximating those shown in Figure 1. Since it is unlikely that any TCC plant charging sweet gasoils would encounter activities lower than 26 A.I., even with the minimum of makeup required to replace attrition losses, this activity has been selected as a base for the present economic study. Higher activities may be obtained by appropriate increases in catalyst makeup rates. Thus, for the present study, we have considered yields from catalysts ranging in activity from 26 to 36 A.I. in increments of 2 A.I. This range in activity calls for makeup rates in the range of 0.1

pounds per barrel of feed stock to greater than 2.0 pounds per barrel (equivalent to 0.5 tons per day to greater than 10 tons per day for a 10,000-barrel-per-stream-day TCC plant). The makeup rate for the 34 A.I. catalyst was obtained by extrapolating the curve in Figure 1.

A portion of the catalyst removed daily for replacement consists of catalyst fines. This material will not normally amount to more than 0.1 pounds per barrel of feed stock, but its elimination is required to maintain the unit in proper operating condition.

A simple system of elutriation and cyclone separation is used to remove the fines from the plant. A portion of the regenerated catalyst stream is continuously by-passed through an elutriator where free-falling catalyst is countercurrently contacted with a stream of air which carries the fine material overhead and into a cyclone separator from which they are withdrawn into a fines storage hopper. The catalyst pellets emerge from the bottom of the elutriator free of fines and flow back into the main catalyst stream by gravity.

Thus, it is seen that the minimum catalyst makeup would be that quantity required to replace the fines. Where greater catalyst makeup rates are used, it is apparent that heavier elutriation would be desirable for removing all catalyst withdrawn. This is the recommended procedure and is accomplished by increasing the air rate through the elutriator until the desired quantity of catalyst is carried overhead into the cyclone separators. By this procedure the catalyst within the plant will be of maximum particle size and free of fines and fragments of broken pellets.

TABLE 1

Summary of Yields—Catalyst Activity vs. Product Distribution

TYPE CATALYST	Clay Catalyst					
Catalyst Activity Index—Cat-A Method	26	28	30	32	34	36
Type Operation	Single Pass					
Operating Conditions:						
Space Velocity V/Hr/V	0.35	0.35	0.5	0.74	1.05	1.34
Avg. Reactor Temp. °F	850	850	850	850	850	850
Avg. Reactor Pres. psig	10	10	10	10	10	10
Steam, Wt. Percent of Charge	5	5	5	5	5	5
Cat/Oil Ratio, Vol/Vol	1.8	1.8	1.8	1.8	1.8	1.8
Conversion (100—Vol. Percent Total Catalytic Gas Oil)	55.6	61.5	62.7	63.6	64.7	65.8
Yields:						
Motor Gasoline, C_4 Free—Vol. Percent	43.7	46.2	48.1	49.5	50.5	51.7
Light Catalytic Gasoil (No. 2 Fuel)—Vol. Percent	28.1	26.6	25.9	25.5	25.0	24.3
Heavy Catalytic Gasoil—Vol. Percent	16.3	11.9	11.4	10.9	10.3	9.9
Total C_4—Vol. Percent	11.6	13.2	12.6	12.4	12.8	13.1
Recovery—Vol. Percent	99.7	97.9	98.0	98.3	98.6	99.0
Dry Gas—Weight Percent	6.3	7.6	7.3	7.0	6.9	6.7
Coke—Weight Percent	3.5	4.3	4.3	4.3	4.3	4.3
Coke Burned lb/Hr/10,000 BPSD Chg	4,460	5,500	5,500	5,500	5,500	5,500
N-Butane—Vol. Percent	1.6	1.7	1.6	1.5	1.5	1.6
I-Butane—Vol. Percent	6.6	7.0	6.4	6.0	6.0	6.4
Butenes—Vol. Percent	3.4	4.5	4.6	4.9	5.3	5.1
Total C_4—Vol. Percent	11.6	13.2	12.6	12.4	12.8	13.1
10lb Motor Gasoline—Vol. Percent	47.4	50.1	52.1	53.6	54.8	56.0
Excess C_4—Vol. Percent	7.9	9.3	8.6	8.3	8.5	8.8
Dry Gas F.O.E.—Vol. Percent	6.4	7.8	7.5	7.1	7.0	6.8
Catalyst Make-Up Tons/Day	0.5	1.25	2.4	4.9	10	.....
Catalyst Make-Up Cost $/Day	40	100	192	392	800	.....

Yields vs. Catalyst Activity Index

Table 1 presents yields from cracking the Mid-Continent stock in single-pass operation over clay catalysts whose activities vary from 26 to 36 A.I. These data are also given in graphic form in Figure 2. In selecting these yields the following conditions were fixed:

Average Reactor Temperature	850° F.
Average Reactor Pressure	10 psig
Steam	5% Wt. of Charge
Catalyst/Oil Ratio V/V	1.8
Coke Yield	4.3 Wt. %

The average reactor temperature was fixed at 850° F. since this level is favorable from the standpoint of gasoline yields, gasoline quality and liquid recoveries. The 10 psig reactor pressure is conventional, and 5 percent weight of steam is an amount which assures complete vaporization of the charge stock at prevailing conditions of temperature and pressure. The catalyst-to-oil ratio was fixed at 1.8 to correspond with 100-tons-per-hour catalyst elevators on a 10,000-barrels-per-stream-day plant. Coke make was fixed at 4.3 percent weight of charge which corresponds to a burn-off rate of 5500 pounds per hour in the kiln.

As the catalyst activity was varied, the space rate was changed to obtain the proper conversion for 4.3 percent weight of coke so as not to exceed the stated capacity of the kiln. It will be noted, however, that it was not possible to obtain 4.3 percent coke with the 26 A.I. catalyst at 850° F. even though the minimum practical space velocity of 0.35 was used. This fact immediately points out the undesirability of using low catalyst activities since it is then necessary to use excessvely high temperatures or extremely low space rates, either or both of which result in unfavorable product distribution, particularly from the standpoint of high gas formation and low liquid recoveries.

Figure 2 emphasizes the advantages to be gained from cracking with catalyst of high activity. As activity increases from 28 to 34 A.I. at constant coke yield, the debutanized gasoline yield increases from 46.2 to 50.5 volume-percent of fresh charge. This represents an increase of 9.3 percent based on gasoline yield. At the same time the cracking efficiency, which is defined as $\frac{\text{gasoline} + \text{total } C_4}{\text{conversion}}$, increases from 96.6 to 97.8. These same data are shown in the following tabulation where results are also given on the 34 A.I. catalyst when operating conditions are adjusted to give the same gasoline yield as that obtained from the 28 A.I. catalyst.

Activity Index of Clay Catalyst	28	30	32	34	34
Conversion (100—Vol. % Cat. Gasoil)	61.5	62.7	63.6	64.7	53.6
Gasoline C_4 Free—Vol. % Chg	46.2	48.1	49.5	50.5	46.2
Total C_4—Vol. %	13.2	12.6	12.4	12.8	9.1
Liquid Recovery—Vol. %	97.9	98.0	98.3	98.6	101.7
Coke—Weight %	4.3	4.3	4.3	4.3	2.6
Cracking Efficiency—Vol. %	96.6	96.8	97.3	97.8	103.1

Cracking efficiency and coke yield are markedly improved when using the higher activity and running to the same gasoline yield. Thus, the cracking efficiency has increased from 96.6 to 103.1 and the coke yield has decreased approximately 40 percent—i.e., from 4.3 to 2.6 weight percent of charge. These differences are quite large and have a pronounced effect on economics.

The yields given in Table 1 were used as a basis for calculating earnings.

Earnings vs. Catalyst Activity

Table 2 presents a summary of differential earnings versus catalyst activity. Since we are considering a single plant, the investment is the same in all cases and need not be considered. A direct operating cost of $1000 per day has been assigned to cover all items

TABLE 2

Summary of Differential Earnings vs. Catalyst Activity

CATALYTIC ACTIVITY	¢/Gal.	$/Bbl.	26 A.I.		28 A.I.		30 A.I.		32 A.I.		34 A.I.		36 A.I.	
			B/Day	$/Day	B/Day	$/Day	B/Day	$/Day	B/Day	$/Day	B/Day	$/Day	B/Day	$/Day
CREDITS:														
Motor Gasoline 10lb RVP	6.25	2.625	4,710	12,419	5,010	13,126	5,210	13,650	5,360	14,043	5,480	14,358	5,600	14,672
No. 2 Furance Oil	3.75	1.575	2,810	4,412	2,660	4,176	2,590	4,066	2,550	4,004	2,500	3,925	2,430	3,815
Heavy Catalytic Gasoil	.....	0.97	1,630	1,581	1,190	1,154	1,140	1,106	1,090	1,057	1,030	999	990	960
Excess C_4 Cut F. O. E.	.....	0.97	530	514	633	614	581	564	561	544	571	554	569	552
Dry Gas F. O. E.	.....	0.97	643	624	775	752	745	723	714	693	704	683	684	664
Total Credits	.....	.....	.....	19,550	.....	19,822	.....	20,109	.....	20,341	.....	20,519	.....	20,663
DEBITS:														
Fresh Charge Stock	3.5	1.47	10,000	14,700	10,000	14,700	10,000	14,700	10,000	14,700	10,000	14,700	10,000	14,700
Direct Operating Cost Excluding Catalyst Cost	.....	.....	.....	1,000	.....	1,000	.....	1,000	.....	1,000	.....	1,000	.....	1,000
Total Debits Excluding Catalyst Cost	.....	.....	.....	15,700	.....	15,700	.....	15,700	.....	15,700	.....	15,700	.....	15,700
Catalyst Make-Up	.....	.....	0.5*	40	1.25*	100	2.4*	192	4.9*	392	10*	800	.....	.....
Total Debits Including Catalyst Cost	.....	.....	.....	15,740	.....	1,5800	.....	15,892	.....	16,092	.....	16,500	.....	.....
Credits Less Debits Excluding Catalyst Cost	.....	.....	.....	3,850	.....	4,122	.....	4,409	.....	4,641	.....	4,819	.....	4,963
Credits Less Debits Including Catalyst Cost	.....	.....	.....	3,810	.....	4,022	.....	4,217	.....	4,249	.....	4,019	.....	.....
Differential Earnings Excluding Catalyst Make-Up Cost	.....	.....	.....	Base	.....	272	.....	559	.....	791	.....	969	.....	1,113
Differential Net Earnings Including Catalyst Make-Up Cost	.....	.....	.....	Base	.....	212	.....	407	.....	439	.....	209	.....	.....
Differential Catalyst Make-Up Cost	.....	.....	.....	Base	.....	60	.....	152	.....	352	.....	760	.....	.....

* Tons per day.

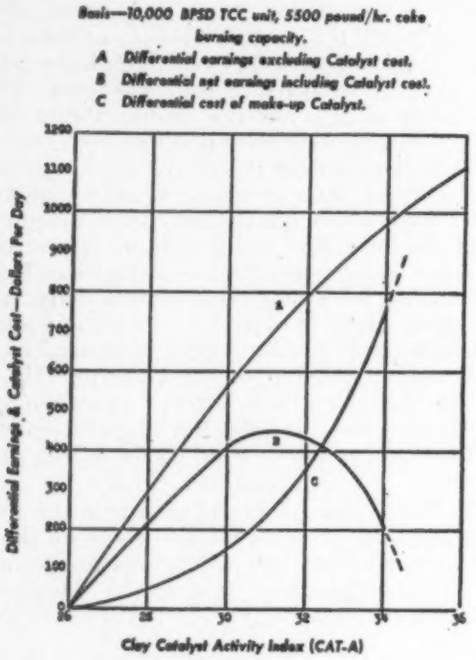

FIGURE 3

Differential earnings vs. catalyst activity.

other than catalyst cost, and the catalyst cost is given as a separate item.

The following price structure was chosen:

	Cents per Gallon	Dollars per Barrel	Dollars per Ton
Charge Stock	3.5	1.47	....
10lb Catalytic Motor Gasoline 78 ASTN Octane Number	6.25	2.625	....
No. 2 Furnace Oil	3.75	1.575	....
Heavy Catalytic Gas Oil	....	0.97	....
Fuel Oil	....	0.97	....
Clay Catalyst Cost	....	....	80.00

Results are expressed in terms of differential earnings per day above a base catalyst activity of 26 A.I. and are given without catalyst makeup cost and again including catalyst cost in order to show more clearly the relation between catalyst activity and earnings.

Figure 3 presents curves constructed from the data in Table 2. Curve A shows differential earnings excluding catalyst cost. Curve B shows differential net earnings including catalyst cost, and Curve C shows diqerential catalyst cost—all plotted against catalyst-activity index. The differential earnings (Curve A) are reduced by the cost of catalyst (Curve C) to the final differential net earnings shown by Curve B. The differential net earnings increase steadily from 26 A.I. catalyst to attain a maximum at 30-32 A.I. catalyst and then decrease rapidly above 32 A.I. due to the excessive catalyst makeup rates required to obtain the higher equilibrium activities.

The shape of Curve A (Figure 3) is well worth noting since it again illustrates the advantages to be derived from the use of high-activity catalysts. The rise in value of products with increase of catalyst activity is a reflection of the improved product distribution which was shown graphically in Figure 2. With very low catalyst activities, the cracking reaction must be forced by the use of high temperature or high catalyst-to-oil ratios, resulting in undesirable thermal reactions which result in low cracking efficiency. The demonstrated sensitivity of product value to catalyst activity and the opposing influence of catalyst cost to attain the higher activities illustrates the importance of design and operating technique on earnings in catalytic cracking processes.

Conclusion

The results of this economic study lead to conclusions which are stated briefly as follows:

1. Earnings increase with increase in equilibrium catalyst activity due to better cracking efficiency with the higher catalyst activities.

2. A minimum catalyst makeup rate is not necessarily the optimum operation since earnings may not be at a maximum.

3. Maximum earnings are realized at a clay catalyst activity level of 30-32 A.I., corresponding to a catalyst makeup rate of approximately 4 tons per day in the case of a 10,000-barrels-per-stream-day TCC plant. This is equivalent to 0.8 pounds of catalyst per barrel of total feed. Obviously, this conclusion depends on the catalyst activity level for a makeup rate of 4 tons per day. In cases where higher catalyst activities are realized for this same makeup rate, then the optimum activity will be at the higher level.

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Physical Chemistry of Lubricating Oils

Part III—OPTICAL AND ELECTRICAL PROPERTIES

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THE recognition of the nature of light as electromagnetic alternating field is by now so general that no explanation is needed for the heading of this chapter. Light is but a small fraction of the long spectrum of electromagnetic waves extending from the γ-rays to the long radio waves in a continuous line of increasing wave lengths (or decreasing frequencies). The interaction of these fields with the various particles of our universe depends on size and charge of the particles on the one hand and on the frequency (or wave length) of the "wave" on the other. Each particle will oscillate in resonance with that particular wave out of the entire spectrum which happens to have a frequency identical with the natural frequency of the particle (or the corresponding overtones). As such resonator the particle will absorb a portion of the energy radiated upon it and either transform it into heat or otherwise "dispose" of it. Examination of a spectrum of a radiation source before and after transmission through a substance will therefore show with which part of the spectrum the particles of that substance are swinging in resonance. The laws of mechanics, which tell us that the natural frequency of any part of a system is the higher the smaller its mass and the stronger its binding force, apply here too, and we can deduce from the frequencies of the "absorption bands" what particles are contained in our substance. The valence electrons of the atoms, from which the smallest particles—the molecules—of lubricating oils are made up, resonate with waves of high frequency in the ultraviolet and visible light portion of the spectrum, "producing" the color of oils in the latter. The atoms resonate with the infrared (or heat) waves. The molecules as a whole will interact, if they contain dipoles (v.s.), with waves of radio frequency, producing thereby an effect commonly known (and feared) as "dielectric loss" or power factor. We shall deal with the interaction of electro-magnetic fields and lubricating oils in the sequence of frequencies indicated.

IV.1 The Measurement of the Color of Lubricating Oils

The color of lubricating oils has in the past—and often still today—been determined by comparison with the color of standardized glasses or solutions, and sometimes (in the white-oil industry) by comparison with "standard" oils which have been selected by arrangement on the basis of "easily" discernible color steps. As the color of lubricating oils is not a very important physical property, only little work was done to improve on this unsatisfactory state of affairs. The patient experimental work of Koetschau[85] and others (apparently working independently of each other!) is slowly leading the way to a more adequate method of color measurement. The fundamental principles underlying such measurement are quite simple:

For most oils the relationship between the relative light transmission I/I_o and the thickness D of the layer through which the light passes, as well as the concentration c (in measurements of undiluted oils $c = 1$), is given by Lambert-Beer's law.

$$\ln \frac{I}{I_o} = -K \cdot D \cdot c \qquad (1)$$

where I/I_o = intensity of incident and transmitted beam of light, respectively. K = extinction coefficient. This law holds irrespectively of the wave length of the light chosen; K varies, of course, with the wave length of the light. Deviations from equation (1) occur whenever the liquid under test dissipates light by scattering. This may be due to strong fluorescence or the presence of colloidally dispersed particles. For oils containing such particles K is not independent of D and C, meaning that different values of K will be obtained, depending on the size of the cell containing the liquid and on the degree of dilution to which the liquid may have been subjected. The concentration of fluorescing and of colloidally dispersed matter is in most ordinary lubricating oils not high enough to affect the applicability of equation (1). Caution should, however, be observed in the extrapolation of data of diluted oils, and the applicability of (1) tested on every case by proving the linearity of the log I/I_o vs. concentration curve.

The human eye responds to the intensity of light (transmitted by the sample) more nearly logarithmically (that is proportionally to K) than linearly. It is therefore regrettable that the D-2 committee of the ASTM decided to propose percentage transmission as measure of the intensity of color instead of the extinction coefficients.

If all oils had the same color, but varied only in the depth (intensity) of that color, the extinction coefficient determined at white (day) light would suffice as datum. But this is—as many a laboratory technician observed with dismay—not the case. The hue of oils varies all the way from yellowish (green) to purplish and brownish red. Were the coloring bodies in oils ordinary dyestuffs, the color of each sample could be defined by the wave length of its absorption maximum and the corresponding K value. But such selective absorption has (in the visible spectrum) never been observed in lubricating oils. Their absorption vs. wave length (λ) curves are always continuous, Figure 19. The relative absorption distribution in the blue and red parts of the

spectrum determine the hue of the oil's color. This will become more readily recognizable by changing the mode of plotting K vs. λ, as has been proposed by Lederer.[89] From theoretical considerations this author derived an expression for the continuous part

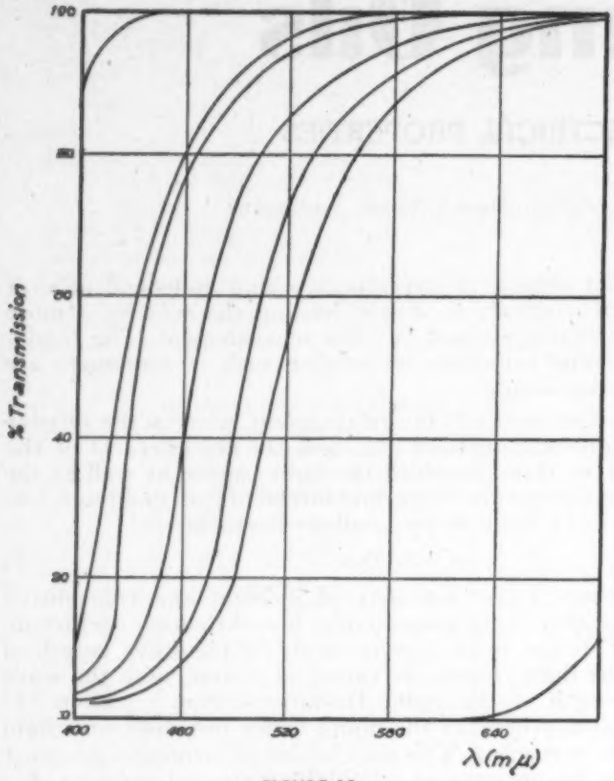

FIGURE 19

Transmission vs. wavelength curves of a series of oils (degree of refining increases from right to left) from ref. (120).

of any absorption spectrum (at a reasonable distance from the next selective absorption band):

$$\ln \frac{I}{I_o} = D \cdot A \cdot \kappa \cdot \frac{\lambda}{I + \left(\frac{\kappa}{\lambda}\right)^2} \cdot e^{-(\lambda/\kappa)^2} \qquad (2)$$

where A = a factor proportional to the number of excited oscillators
κ = a damping factor
λ = the wavelength at which the observation I/I_o is made

For lubricating oil e.g. (2) could be simplified to the form

$$\ln \frac{I}{I_o} = K = D \cdot A \cdot e^{-(\alpha' - \beta'/\lambda^2)} \qquad (3)$$

where α' and β' are constants. From equation (3) follows that log K plotted vs. $1/\lambda^2$ should give a straight line. This is indeed the case, (See Figure 20). The data of Johnson and Garcia[86] show a systematic deviation at the lowest wavelengths, which is obviously due to the fact that the white oil, which they used in the reference cell, has not zero but a finite absorption at $\lambda = 410 m\mu$. The slope of the absorption curve in this chart is a measure of the hue of the oil. The steeper the angle, the more "yellowish" is the oil, the more oblique the angle the more "reddish" is the oil. The depth of the color is indicated by the value of K (or log K) at a certain wave length. Lederer proposed to use the value of log K at $\lambda = 530 m\mu$ (which is reasonably close to the point of maximum sensitivity of the human eye and the energy maximum in the visible spectrum of white sunlight) as standard measure of color depth. Determination of absorption with two—preferably three—narrow-band filters would, therefore, with the help of the Lederer chart, permit complete color characteristic of an oil. Deviations from the straight line (usually accompanied by extreme obliqueness of slope) will immediately indicate presence of colloidally dispersed materials—such as asphalt—in an oil.

The simplicity, and at the same time theoretically sound approach of this method to the problem of lubricating oil color measurement, has not been reached by any of the subsequent investigators.[86, 87, 88] Most of these either ignored or overlooked Lederer's work. Koetschau came close to it by using the slope $\Delta \log K/\Delta\lambda$ between 470 and 570 $m\mu$ as a measure of the hue of the oil. Diller and collaborators (whose work was subsequently proposed by the ASTM) use also two (or three) filters of different wave length in a photoelectric colorimeter: a "violet" filter of dominant wave length $\lambda = 446 m\mu$, a "North Sky" wide-band filter of dominant wave length $\lambda = 496 m\mu$, and a "Red" narrow-band filter of $\lambda = 624 m\mu$. They define the "photoelectric color" as the percent transmission when using the "North Sky" filter, or for white oil when using the "Violet" filter as $90 + \frac{\%\ \text{Transmission}}{10}$

These authors found that the vast majority of lubricating oils show a relationship between the transmission with the "North Sky" filter and the "Red" filter (or with other words, a fairly narrow range of slopes in the Lederer diagram). They propose to call the hue of an oil "greenish" or "reddish" by the amount that it deviates from the medium line of Figure 21, and suggest to simply call the hue of an oil falling outside the shaded area as "abnormal." Both this empirical measure of the hue, and the use of the wide-band "North Sky" filter seem to the reviewer as designed to appeal to a spirit of limited understanding of physical principles, which is actually on its complete way out of the petroleum-testing laboratory. Once they had so ably shown the fundamental inadequacy of the conventional colorimeter for true color measurement, they should have gone all the way in abandoning even the attempt to connect the new colorimeter readings with the old. The use of the proposed wide-band filters does only unnecessarily complicate inter-comparison of their transmission with spectrophotometer curves.

IV 2.
Nature of Coloring Substances in Lubricating Oils.

The hydrocarbons, which constitute the major portion of the components of lubricating oils, are all colorless, or practically so, up to the highest molecular weights studied. The only colored hydrocarbons are those containing a large number of conjugated or cumulated double bonds and condensed aromatic ring systems containing more than four rings. None of

TABLE 30

Ultimate Analysis of Petroleum Resins

ORIGIN	Resin Content of Oil Percent	d_4^{20}	$\overline{M}$	% C	% H	% O	% S	Sup. N.	Ref.
Penna. SAE 40	3.7	1.000	583	87.19	11.06	1.03	0.72	2.69	92
Colombian SAE 40	3.9	1.068	456	85.51	10.04	2.18	2.27	4.77	92
Roumanian SAE 40	2.0	1.078	406	80.25	9.95	7.40	2.40	10.8	92
German Distillate (SAE 10) P	1.3	.....	525	83.45	9.34	5.03	2.18	.....	*
Same N	.8	.....	520	78.09	10.77	5.64	5.50	.....	*

* E. Haus, Oel u Kohle 14, 299 (1938).

these have ever been found in natural petroleum derivatives. The many hydrocarbons resembling petroleum lubricants in physical and chemical properties, which have been synthesized here and abroad during the past decade, were all essentially colorless. The molecular weights of these synthetic hydrocarbons ranged in all classes paraffinic, naphthenic and aromatic—up to about 600. Schindler and Bondi[90] separated by selected adsorption out of a number of residual cylinder oils up to 85 percent (weight) of practically colorless hydrocarbons in the molecular weight range 600 to 800. The balance (15 percent) were resinous products, the so called "petroleum resins" which other investigators[91,92,93,94] found to consist mainly of oxygen and sulfur compounds of so far entirely unknown constitution. Viscosity and molecular weights (see table of Section III) indicate that these resins are polycyclic compounds. But how the oxygen and sulfur is combined with these structures has not yet been investigated. Typical ultimate analyses are presented in Table 30. By saying—as Marcusson did—that these substances seem intermediate between hydrocarbons and asphalts, little additional light is shed on their nature. The resinous adsorbates from oxidised oils, which will be discussed in Section VII, differ from the natural resins significantly in composition. The course of oxidation of hydrocarbons to resins must therefore—if such took place at all— have varied considerably from the methods used in the laboratory. The writer has, indeed, reason to be-

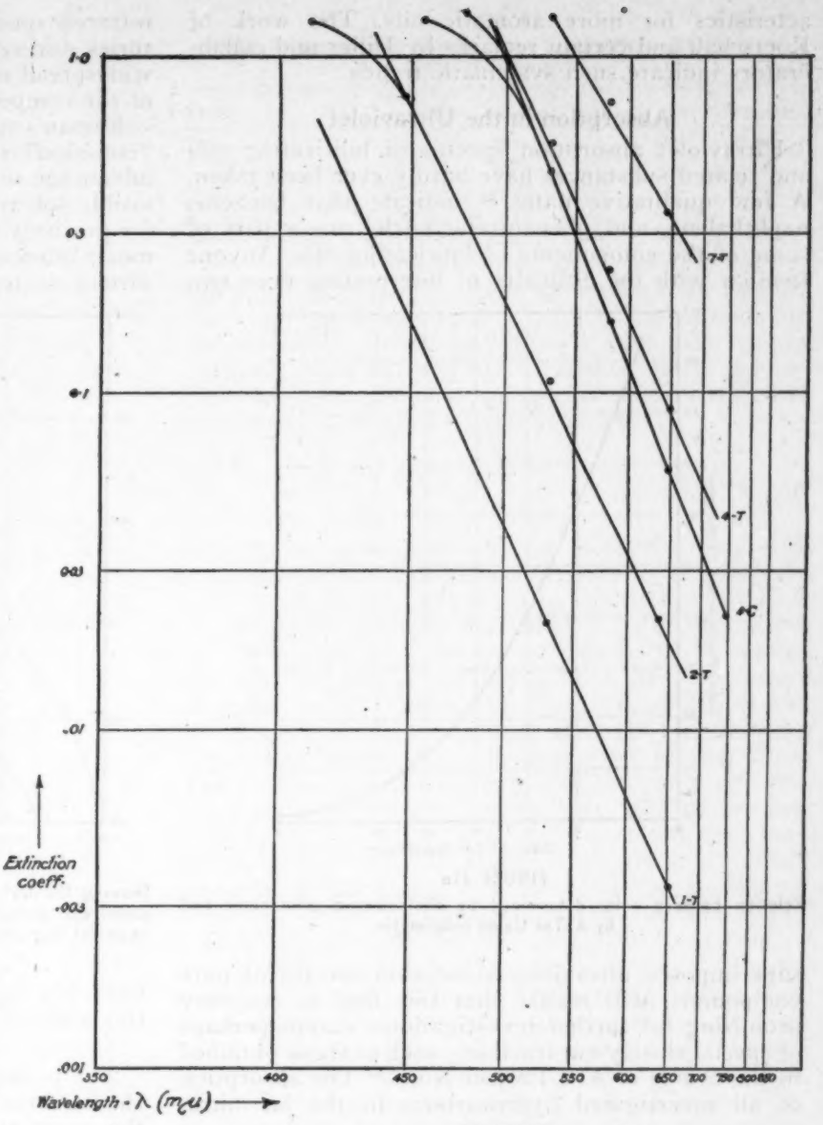

FIGURE 20

Lederer graph for logarithm of extinction coefficient of lubricating oils vs. (1/wavelength)^2.

The lines are from data of Johnson and Garcia.[86]

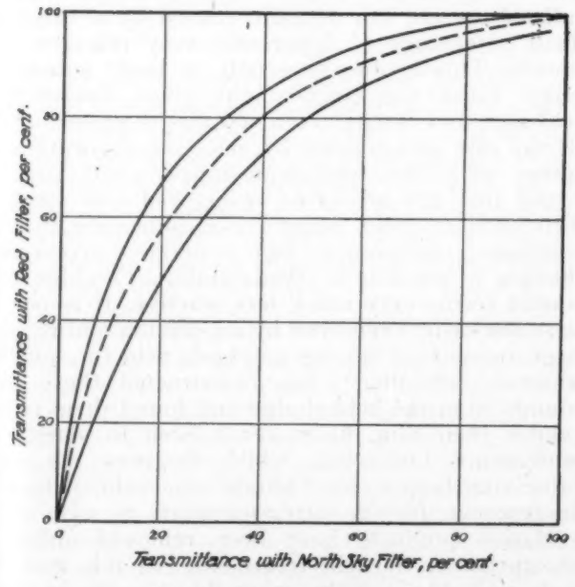

FIGURE 21

Typical relationship between transmittance in red and north-sky filter for lubricating oils. Deviation from the broken line determines the hue of an oil. (from ref. 87).

lieve that the opposite course has been followed by nature, that hydrocarbons originate in the "resins." The optical properties of these resins have been discussed by Koetschau. A general correlation between overall composition—as signified by the Viscosity-Pole-Height W_P—and the slope of the log K/λ curve is illustrated on Figure 23.

The trend, increasing steepness of absorption wave length curve with increasing paraffinicity, becomes especially apparent for the resin-free "bright oils," the hydrocarbon portion of lubricating oils. The presence of petroleum resins, the color of which depends mostly on their functional groups tends to suppress the differentiating effect of the dominant hydrocarbon group of these oils.

The assumptions made in the derivation of equations (2) and (3) that no selective absorption occurs in the immediate neighborhood of the visible spectrum (in the ultraviolet) is certainly not quite correct for aromatic oils, and continued spectrophotometric investigation of lubricating oils are bound to lead to the observation of systematic slope char-

acteristics for more aromatic oils. The work of Koetschau and certain remarks by Diller and collaborators indicate such systematic trends.

Absorption in the Ultraviolet

Ultraviolet absorption spectra of lubricating oils and related substances have hardly ever been taken. A few qualitative data[95,96] indicate that benzene, naphthalene, and phenantrene nuclei are a part of some of the components of lubricating oils. Anyone familiar with the difficulty of interpreting even two superimposed ultraviolet absorption spectra of pure compounds, will realize that this field is not very promising for further investigations, except perhaps of special closely-cut fractions, such as those obtained in the course of API-Project No. 6.[97] The absorption of all investigated hydrocarbons in the far ultraviolet (at $\lambda = 1200$ to 1600 Å) has been successfully interpreted as due to lifting out of the most weakly-bound valence electron in the molecule, i.e., ionization.[98] The significance of this will become more clearly understood in Chapter IV.6.

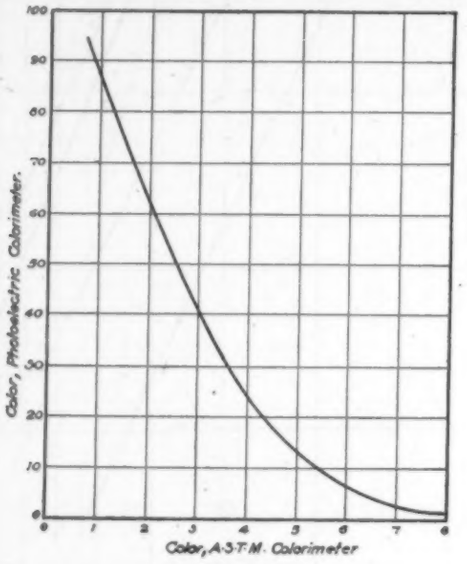

FIGURE 21a

Relation between color determined by photoelectric colorimeter and by ASTM Union colorimeter.

Infrared Absorption and Raman Spectra

Absorption in the infrared is due to the interaction of light waves with those vibrations which the atoms of a molecule perform relative to each other. The characteristic frequencies of vibration of various atom combinations can be calculated in a relatively simple manner[99] from their masses, configuration, and force constants. The state of aggregation affects the infrared absorption spectrum but very little. There is, indeed, no portion of the absorption spectrum as well understood at present as the infrared. It would lend itself therefore ideally to the examination of the average constitution of lubricating oil hydrocarbons. A hopeful beginning has been made by the work of the Bureau of Standards.[100] These workers were able to determine from the extinction coefficients in the spectral range 1120-1850 mμ (8900 to 5400$_{cm}^{-1}$) the percentage respectively of primary, secondary, tertiary and aromatic carbon atoms per molecule (as will be more fully discussed in Section V of this series). The introduction of infrared spectrometry into many petroleum laboratories during the war is bound to bring forth more widespread use of this new tool for the investigation of the composition of lubricating oils.

Raman's technique for the production of molecular "emission" spectra by "scattering," which has the advantage of operation in the more easily accessible visible spectrum, is not applicable to lubricating oil for precisely that reason. The absorption of light by most lubricating oils in the visible region is so strong as to virtually obliterate the feeble Raman lines, not to mention the time-consuming nature of this method.

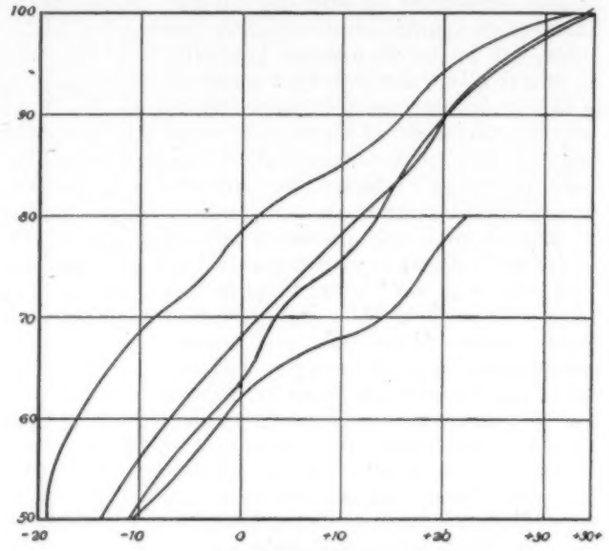

FIGURE 21b

Showing the lack of relationship between photoelectric color (vertical scale) and Saybolt color numbers (horizontal scale) for oils of various chemical composition as exemplified by the various curved lines. (from ref. 87).

IV.3 Fluorescence

The brilliant fluorescence extending over all color shades from purplish blue to dark green is one of the most striking properties of petroleum derived lubricating oils. It is not an inherent property of the bulk of the oil, but actually caused by a relatively small percentage of apparently very reactive compounds. This applies especially to those substances which cause the much-sought green fluorescence. Schindler and Bondi[38] removed this component from all the oils investigated by selective absorption together with the "petroleum-resins," and also observed that the recovered resins had lost much of their brilliant green fluorescence, indicating that the fluorescing compounds had undergone irreversible changes in the course of adsorption. The blue component seems very much less reactive. It is not (at least not easily) removed by adsorption and requires large amounts of fuming sulphuric acid for complete removal. Schindler[101] has re-extracted these compounds from the acid sludge and found them to still exhibit their blue fluorescence even in small concentrations. Oxidation, which destroys the green fluorescing bodies only "blinds" (quenches) the blue fluorescence, for the latter reappears as soon as the oxidation products have been removed either by adsorption or by acid treatment. All this makes it quite probable that the green fluorescence is caused by aromatic non-hydrocarbons, while the blue to purplish fluorescence has its origin in hydrocarbons (and sulfur compounds) containing four or more

condensed rings. The quenching action of nitronaphthalene, picric acid and related substances points into the same direction, since—as is well known—these form molecular (association) compounds with aromatic hydrocarbons. Association compound formation leads as a rule to quenching of fluorescence.[102] Fluorescence spectra from which the nature of the compounds causing it could be fairly well guessed, have never been taken of lubricating oils.

From the evidence presently available fluorescence measurements could hardly be expected to advance our understanding of the chemistry of lubricating

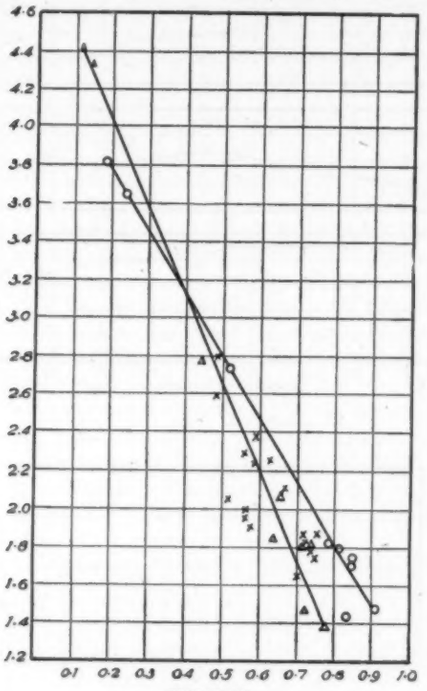

FIGURE 23

Linear relation between Viscosity-Pole-Height W_p and the logarithm of K/W_p

Where K = extinction coefficient ratio for wavelengths 5641A and 5780A;
Δ = Base oils;
° = "Bright oils" (base oils freed from petroleum resins);
x = Conventional motor oils. (From reference[94]).

oils to any considerable extent, and could at best serve for identification purposes. The "quantitative" determination of asphalt or oxidation product concentration in lubricating oils by fluorometry as had been proposed a few years ago[102a] is based on too many unsafe assumptions as to color and quenching effect of the sought substance to be of practical value, and for research work there are more reliable methods presently available.

IV.4 Refractive Index and Optical Rotation

The refractive index of liquids has, due to the ease with which it is determined and due to its relatively clear-cut theoretical interpretation, for many years enjoyed great popularity among organic chemists. Its introduction into analytical petroleum chemistry, and particularly the chemistry of lubricating oil fractions[103,104,105,106,107,108] has advanced our understanding of the composition of these materials very considerably. A brief survey of the various derived functions of the refractive index appears therefore in order.

The refractive index, defined as the ratio of the velocity of light in vacuum to the velocity of light in

TABLE 31

Molar Refraction Increments (from S. Glasstone, Textbook of Physical Chemistry)

ATOM	$[R]_\alpha$	$[R]_D$	$[R]_\beta$	$[R]_\gamma$	$[R]_\alpha$-$[R]_\gamma$
Carbon	2.413	2.418	2.438	2.466	.053
Hydrogen	1.092	1.100	1.115	1.122	.030
Oxygen (in CO group)	2.189	2.211	2.247	2.267	.078
Oxygen (in ethers)	1.639	1.643	1.649	1.662	.023
Oxygen (in OH group)	1.522	1.525	1.531	1.541	.019
Double Bond	1.686	1.733	1.824	1.893	.207 !
Triple Bond	2.328	2.398	2.506	2.538	.210 !

the medium, of hydrocarbons varies between 1.33 for the light paraffines and 1.7 for some anthracene derivatives. Lubricating oils as a rule have values between about 1.47 and 1.54. The most useful expression (for the analyst) is the specific refraction r, first derived by Lorenz and Lorentz in 1880:

$$r_{\lambda,t} = \frac{n_\lambda^2 - 1}{n_\lambda^2 + 2} \frac{1}{d} \qquad (5)$$

which when multiplied with the molecular weight M is shown as molecular refraction $[R]^\lambda$. The theoretical considerations which led to expression (5) lead to the conclusion that the value of [R] determined at $\lambda \to \infty$ represents the actual volume of the molecules in one mol of substance. (As this conclusion is based on the assumption that the molecules are perfectly conducting spheres this will be a poor approximation for the molecules in lubricating oils). The data in Table 31 indicate that the value of r and bond increments is, however, little affected by the form of the molecules. We shall see in the next section how this fact can be made use of in the bond analysis of lubricating oils. Table 31 gives a list of some important mol refraction increments. The molar refractivity of a mixture $[R]_{1,2}$ is given by

$$[R]_{1,2} = x_1 [R]_1 + x_2 [R]_2 \qquad (6)$$

where $x_{1,2}$ = mol fractions. This simple rule permits the calculation of [R] of an otherwise too dark or solid solute from the [R] of solvent and solution. The data in Table 31 indicate that the value of r and [R] depends on the wave length λ of the light which has been used for the measurement. The relationship between r and λ (or better the frequency ν) is given to a good approximation by the relationship:

$$r_\lambda = 1 + \frac{\alpha}{\nu_0^2 - \nu^2} \qquad (7)$$

where ν_0 is the frequency of a characteristic absorption band closest to the frequency ν at which measurement has been performed, α is a measure of the strength of the oscillator of frequency ν. We saw in the previous paragraph that aromatic compounds show a strong absorption band at about 2700 Å while the saturated hydrocarbons absorb selectively only in the far ultraviolet (close to 1600 Å). We should, therefore expect equation (7) to predict a much stronger dependence of n on λ (or ν) for aromatic compounds than for paraffines and naphthenes. This is, indeed, the case. The dispersion, for that is the name of $(n^{\nu_1} - n^{\nu_2})$ — of aromatic hydrocarbons is between two and four times as large as the dispersion of saturated hydrocarbons. The "aromaticity" of lubricating oils can, therefore, be fairly well determined from the specific dispersion $n_\alpha - n_\gamma$ or $[R]_\alpha - [R]_\gamma$, the molar dispersivity, as has been proposed by several investigators.[109,110,111] The values of this constant, given on Table 32, are quite indicative of the degree of sensitivity of the dispersion to the presence of aromatic hydrocarbons. Their quantitative evaluation is hampered, however,

TABLE 32

Specific Dispersion and Aromaticity of Lubricating Oils (Calc. from Data of Ref.[120])

	V-I	Percent Aromatic C.	Percent Rings*	Specific Dispersion
Original Oil	88	9.8	27.2	120
2nd sol.-extract	−35	43.7	55.2	129 (?)
Same, acid-ref'd	−13	37.8	48.2	164
3rd sol.-extract	54	22.0	46.4	116
4th sol.-extract	81	10.3	36.0	118
6th sol.-extract	113	1.5	24.5	97
Same acid ref'd	114	0.2	23.4	88
Raffinate	131	0	16.0	93

* Calculated by Waterman Analysis.

by the fact that condensed aromatic ring compounds increase the dispersion in a rather erratic manner.

Optical Rotation

One of the most interesting optical phenomena is the ability of certain compounds to rotate the plane of polarization of light. This "optical activity" is usually expressed as specific rotation $[\alpha]$

$$[\alpha] = \alpha \ 1 \ . \rho \qquad (8)$$

where α = measured angle of rotation, 1 = length of liquid column (cell in decimeters, ρ = density of substance. $[\alpha] \cdot M/_{100}$ is called the molar rotation (often written [M]). Fresnel (in 1825) recognized that "optical rotation is due to a difference in the

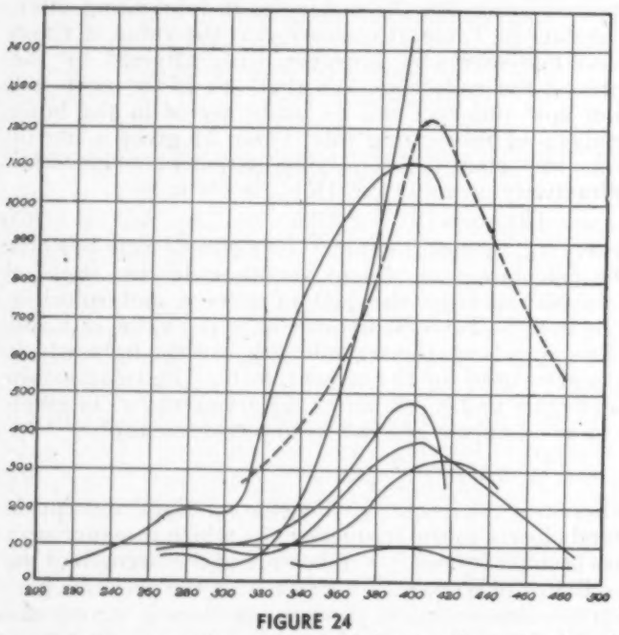

FIGURE 24

Molar rotation of a wide variety of lubricating oils as function of molecular weight of individual fractions. (from ref. 113, except broken line, which was constructed from the maxima of fig. 25). The lowest curve is characteristic of Pennsylvania lubricating oils. The other curves are from Coastal and Mid-Continent crudes.

refraction of right- and left-circularly poralized light in the substance, so that

$$\alpha = \frac{\lambda}{\pi} (n_c - n_r) \qquad (9)$$

where λ = wave length of the light, n_c, n_r refractive index for left and right circularly polarized light respectively.

Very few physical properties have been as thoroughly studied with respect to their significance in terms of chemical structure of the substance exhibiting it as the optical rotation. This was not the least due to the observation that many organic compounds have been found, two of which may be "completely" alike in chemical constitution but rotate the plane of polarized light in different directions (left (l) or right (d)) and, will at the same time react entirely different in physiological processes. Living organisms will often produce substances of but one sense of optical rotation, while most reactions in the laboratory (unless special pains are taken) will result in mixtures containing all the possible "stereo-isomers." The fact that certain fractions of petroleum (especially the lubricating oils) exhibit optical (l)

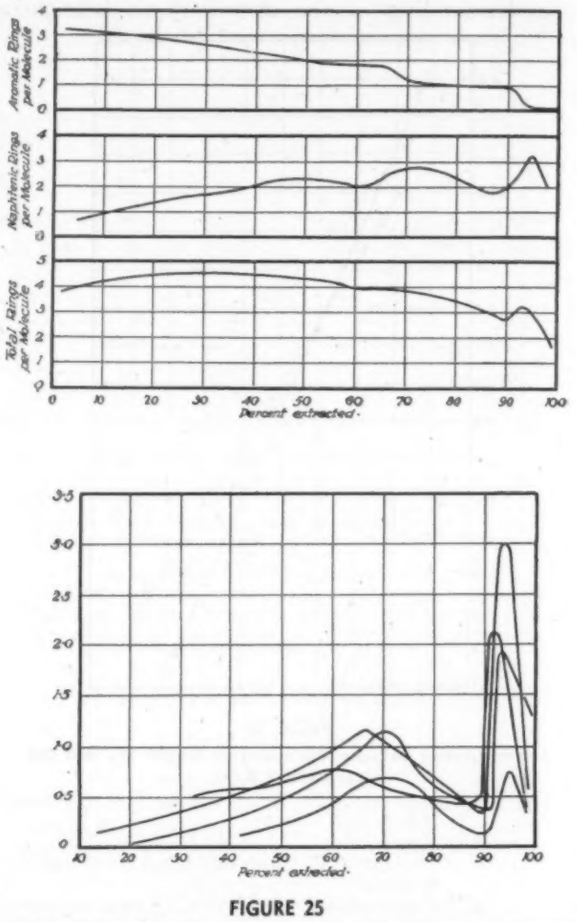

FIGURE 25

Correlation of Chemical Comopsition (upper three frames) and optical rotation (lower frame) as obtained by solvent extractions of a Mid-Continent lubricating oil (from ref. 112).

rotation has therefore been generally considered as proof of the origin of petroleum from living organisms. The exact nature of the lubricating oil components which cause optical rotation is not yet understood. Some of the most recent data[112,113] have been assembled in Figures 24 and 25. There are a number of striking similarities among the rotation-distribution curves of oils of widely varying chemical characteristics (which have already been observed by the authors of reference 112 and 113): The maximum rotation is exhibited by the fraction of 400 molecular weight; the highest concentration of optically active compounds appears to be associated with the presence of naphthenes. The last statement is brought out by the observation that highly paraffinic oils and solvent extracts of any oil investigated show the smallest $[\alpha]$ and [M] in the molecular weight range 380 to 430, while Coastal oils, and especially their naphthenic solvent-fraction of the same molecular weight are characterized by sharp rotation maxima. The wide distribution curves of Figure 24, which

TABLE 33

Dielectric Constants, Molar Polarisations and Dipolemoments of Various Lubricating Oils

OIL	d_4^{20}	η cst	$\overline{M}$	ε	$\frac{2}{\varepsilon}\cdot N_D$	P cm^3	P_E cm^3	μ D.U.	Ref. 116
Solvent Raft	.871	31.5	430	2.186	—.009	139.6	140.5	0	116
Solvent Raft	.867	10.0	306	2.177	—.005	099.5	100.0	0	116
Solvent Extract	1.005	18.5	270	3.103	.640	110.7	88.3	1.04	116
Solvent Raft	.880	13.6	319	2.214	—.002	100.7	100.8	0	116
Solvent Extract	1.009	21.8	283	3.224	.751	119.0	92.2	1.13	116
Conventional Ref	.915	95.5	459	2.293	.012	151.0	150.0	0.22	116
Conventional Ref	.889	.....	426	2.264	.037	142.0	139.1	0.37	116
Conventional Ref	.881	.....	506	2.228	.005	166.8	166.2	0.16	116
Same+4% Rape seed oil	.883	.....	515	2.268	.048	173.2	168.8	0.45	116
Same+12% " "	.886	.....	532	2.345	.129	185.9	173.2	0.82	116
Rape seed oil	.923	.....	854	3.305	1.131	401.9	250.0	2.59	116
Progressively Refined:									
Reddish	.....	.....	.....	2.570	.262	.....	.....	.....	*
Greenish Yellow	.....	.....	.....	2.505	.220	.....	.....	.....	*
Yellow	.....	.....	.....	2.375	.110	.....	.....	.....	*
Light Yellow	.....	.....	.....	2.200	.015	.....	.....	.....	*
Colorless	.....	.....	.....	2.155	—.010	.....	.....	.....	*

* Bull, Oel u. Kohle 11, 499 (1935).

are not materially steepened by even the closest fractionation, preclude the existence of a single compound responsible for the observed optical activity. Most speculations regarding the nature of the active compounds center around hydrocarbon derivatives of the sterols. They are supported by the average molecular weight and the naphthenic character of the active fractions, but cannot explain the broad molecular weight distribution curves of $[\alpha]$. Much additional information regarding the nature of the active group in question could be obtained by determination of the temperature coefficient of $[\alpha]$[114] and of rotatory dispersion. So far $[\alpha]$ of lubricating oils has only been measured at 20° C. and for the Sodium D line.

IV.5 Dielectric Constant and Dipole Moment

In the previous section the refractive index n appeared in an expression, called the Lorentz-Lorenz formula, which presented in the refractivity $[R]^\lambda$ a constant of considerable significance for the analysis of organic compounds. $[R]^\lambda$ is also a measure of the degree to which *electrons* and *nuclei* in a molecule are displaced by an electric field, i.e., polarized. The connection between the polarizability α_P (of non-polar substances) and $[R]^\lambda$ is given by:

$$P_D = \frac{4\pi}{3} N\alpha_P = \frac{r\infty^2 - 1}{r\infty^2 + 2} \cdot \frac{M}{d} \qquad (10)$$

The electronic component P_E of P_D is identical with $[R]^\lambda$ for visible light. The part P_A contributed by the polarizability of the atomic nuclei could be determined by measuring n_λ in the infrared. This is, however, rather awkward. A better method is, to plot the total polarization P, as determined from the dielectric constant ε via

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} \qquad (11)$$

vs. 1/T and taking the intercept of P on the P-axis as P_D. This brings us to the main theme of this section: The dielectric constant ε which is defined as the ratio of the capacity of a condenser filled with the oil to its capacity in vacuum. In the form of equation (11), derived by Clausius and Mosotti, it is a measure of the polarizability of the entire molecule. If the molecules of an oil contain only uniformly distributed electric charges, such as in all paraffinic and most aromatic hydrocarbons, there is no difference between the polarizability of the entire molecule and the polarizability of its component parts—the atomic nuclei and electrons, $P = P_D$. But if the oil contains compounds with non-uniformly distributed electric charges, such as alcohols, acetones, fatty acids and the like, which will orient themselves normal to an electric field imposed on the oil P will be different from P_D. The existence of non-uniform charge distribution (electric *dipoles*) in a molecule changes its behavior in an electric field profoundly, provided the frequency of that field is sufficiently low to permit the dipole to orient itself with the field. The contribution P_0 made by the process of orientation to the total polarization P has been derived by Debye[115] as

$$P_0 = \frac{4\pi}{3} N \frac{\mu^2}{3\kappa T}, \text{ therefore } P = \frac{4\pi}{3} N \left(\alpha_P + \frac{\mu^2}{3\kappa T}\right) = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{d} \qquad (12)$$

where μ = "dipole moment" = elementary electric charge × distance of charge center from center of gravity of the dipole. The dipole moment (as a measure of the "polarity" of an oil) can, therefore, be determined from the temperature coefficient of P or from the difference $P - P_D$ by the relation

$$\mu = .0128 \sqrt{(P - P_D)\, T} \qquad (13)$$

If $P/P_D > 1.2$ it is a fair approximation to replace P_D in equation (13) by $P_E (= [R]_D)$. For smaller values of P/P_D this approximation is not very good, since the difference $P - P_D$ then becomes of the same order of magnitude as $P_D - P_E = P_A$, which can then no longer be neglected. Kadmer[116] and other investigators of the dielectric properties of lubricating oils overlooked this fact, and calculated μ from equation (13). Since for most lubricating oils $P - P_D$ is very small (becoming zero for white oils) the use of such an approximation invalidates many of their calculations. There are too few dielectric-constant/temperature curves of lubricants in the literature[117] to evaluate P_A at present.

When evaluating the data given in Table 33, one should keep in mind two additional points: (a) the dipole moments given are due to a small portion of the lubricating oil only, since, as is clearly shown, the hydrocarbon components of such oils have no dipole moment. The "polar" portion is apparently identical with the "petroleum-resin" fraction, which has previously been described as responsible for the color of lubricating oils and some of their other physical and chemical properties. Viscosity measurements on oil-resin systems[38] indicated that interaction between the hydrocarbon and resin molecules is small. We feel, therefore, safe in deriving from the available data (remembering that μ^2 and not μ are additive!) that petroleum resins have dipole moments of between 1.0 and 2.5 D,* a figure which is in accord with whatever little we know about the chemical structure of these complex substances. (b) Although still too small by the additive constant P_A (~ 5 percent), P_E of the refined oils is often larger than P, which is theoretically impossible. The reason is, that for complicated and non-spherical molecules equation (12) is really not a correct expression of their polarizability. The use of more complicated mathematical forms is, however, not justifiable for such purely phenomenological discussion as here presented. The term "polar compounds" has been used very loosely in the lubricant industry in order to characterize substances which reduce boundary friction by formation of oriented layers on rubbing surfaces. The details of these phenomena will be discussed in Section VI of this series. It shall here only be pointed out that the dipole moment ("polarity") is not a

* D = Debye unit = 1×10^{-18} e.s.u.

measure of the force field or even the presence of functional groups, such as OH, O, S, CO, etc., for it is well possible to completely compensate the unbalanced charges of these groups within one molecule resulting in $\mu = O$, as for instance in carbon tetrachloride; and the surface activity of a polar group is more a function of the "accessibility" of this group than of the magnitude of the dipole moment. Quite a number of additional structural requirements go into the make up of "oiliness" additives which will be discussed elsewhere. The very fact that many polar substances, such as rosin oils[116] and low-molecular-weight ketones, esters, etc.[118] have by themselves and impart to lubricating oils poorer film strength values than are exhibited by pure hydrocarbon oils, demonstrates quite clearly that the dipole moment is only an incidental property, but *not* a characteristic of effective boundary lubricants.

Dielectric Loss

The absorption of energy by liquid dielectrics in the low radio frequency range is a phenomenon which is intimately connected with the presence of polar compounds in such liquids. The dipole molecules carry out rotational oscillations in orienting themselves with the alternating field. The surrounding liquid medium offers a resistance to these motions, which is roughly proportional to its viscosity. The dipoles' characteristic frequency of oscillation (at which the energy absorption becomes a maximum) is usually expressed by its reciprocal value, the relaxation time τ. This constant determines the rate of decay of the average electric moment $\overline{m}$ of the molecules by

$$\overline{m} = \frac{\mu^2}{3\kappa T} F_{oe}^{-t/\tau} \qquad (14)$$

where F = field strength at time t = 0. The dielectric loss (commonly expressed as tan of the angle δ by which the current lags more than π behind the applied potential.

$$\tan \delta = \frac{(\varepsilon_0 - \varepsilon\infty)\chi}{\varepsilon_0 + \varepsilon\infty \chi^2} \text{ where } \chi = \frac{\varepsilon_0 + 2}{\varepsilon\infty + 2} 2\pi\nu\tau \qquad (15)$$

$$\frac{\tan \delta}{\max} = \tfrac{1}{2} \frac{\varepsilon_0 - \varepsilon\infty}{\sqrt{\varepsilon_0 \varepsilon\infty}}, \varepsilon = \varepsilon\infty + \frac{\varepsilon_0 - \varepsilon\infty}{1 + \chi^2} \qquad (16)$$

where ε_0 = dielectric constant under electrostatic conditions, and $\varepsilon\infty = n^2\infty$. The relaxation time τ is strongly temperature dependent, decreasing exponentially with increasing temperature. According to Eyring[36] the temperature function can be written

$$\frac{1}{\tau} = A\, e^{-\Delta E^{\neq}/RT} \qquad (17)$$

where the energy of activation $\Delta E^{\neq}$ has numerical values similar to the same term in the viscosity equation of the liquid under examination. From this follows that the frequency of the current at maximum loss is low at low temperature and high at high temperatures. For the lubricating oils which are ordinarily used as cable oils the absorption maximum is at room temperature near 10^5 cycles per second. The loss factor of new oils in the ordinarily used frequency ranges (~60 cycles) is usually negligible. The oxidation products formed during use of transformer oils increase the loss factor very considerably,[119,120] especially when they appear as colloidal suspensions. Anderson observed after 31 months of transformer operation the following changes of tan δ at 60 cycles and 20° C.: unrefined oil: increase from 10 to 1057 $\times 10^{-4}$, mildly refined oil: from 10 to 30 $\times 10^{-4}$, and over-refined oil (British A-30 type) from 10 to 776 $\times 10^{-4}$. These changes are of a magnitude which even the practical man cannot overlook. In cables, where dielectric loss matters much more than in transformers, oils are not exposed to such radical oxidizing conditions as in transformers. For the latter service the new oil-loss factor can, therefore, be considered most important. It should always be below .5 percent in the anticipated operating temperature and frequency range. Some typical values are given in Table 34. The rather high loss-factor values of some oil-non-hydrocarbon systems cannot be accounted for on the basis of the dipole relaxation theory outlined above. Sometimes the extreme loss is due to conduction—which will be treated in the next paragraph—and often it is due to the existence of a colloidally dispersed phase or a second phase undergoing a first order transition. The mechanism due to which emulsions or suspensions of dipole substances in non-polar media, such as lubricating oils exhibit high dielectric loss factors is not at all understood.[121] The investigations by Piper and collaborators have brought out that metallic soaps in oils cause anomalous dispersion in the neighborhood of the gel-point, while fatty acids, low-molecular-weight alcohols, waxes dissolved in white oils, increase the loss factor in a regular manner, producing no anomalies at the phase-separation temperature, except phenol, which shows a very steep increase at the phase-separation temperature, but returns to normal as soon as the phenol droplets turn into crystals, and cetyl and higher alcohols, the dielectric absorption of which rises steeply at a certain transition temperature independent of whether they are in bulk or suspended as crystals in lubricating oil. A general theory explaining these phenomena has not yet been proposed.

TABLE 34
Dielectric Loss Factors of Various Oils

OIL	d_4^{20}	Vis. at 100° F. cst	$\varepsilon - n_D^{20}$	μ D.U.	Power Factor at 60 Cycles New Oil	85° C. (%) Oxydised Oil*	Ref.
Solvent Extract 2	.9589	72.8	0.085	.485	60.5	150 (30)	"
Solvent Extract 4	.8840	24.8	—0.040	0	.50	24 (290)!	"
Sol. Raffinate.....	.8405	16.5	—0.075	0	.01	0.1 (150)	"

* At an oxygen absorption of 6000 c.c. O_2 (NTP) per kg. of oil, figure in parentheses time in hours to reach this oxygen absorption; all from ref. (120).

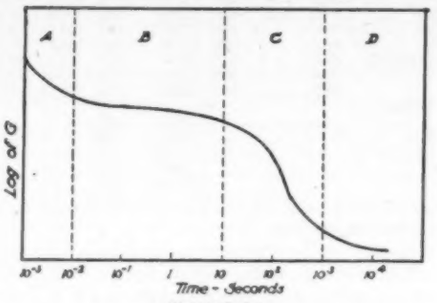

FIGURE 26
Variation of conductance with time at high voltage gradients. (123)

IV.6 Electric Conductivity and Related Phenomena

The electric conductivity of refined lubricating oils is exceedingly small, of the order 10^{-14} mhos/cm³. The numerical values of the conductivity of liquid dielectrics are a function of many factors which are rather uncommon in true conductors. Aside from the expected importance of the preparation of the measuring cell, the conductance is strongly influenced

by the shape of the electrodes (at high potential gradients),[122] by the magnitude of the applied potential gradient (often called "dielectric stress") and the time passed since the start of voltage application.[123] The time effect is of considerable importance in the evaluation of transformer-oil conductivity data. The change of conductance with time is indicated by Figure 26 (from reference 123). "The region A, the brief initial decaying conductance is probably due to the orientation of large dipoles; region B represents the true d-c conductance which is supposed to be due entirely to ions; region C represents the time during which ions are swept out

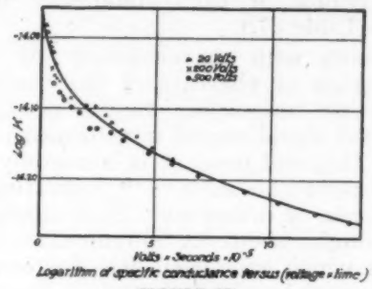

FIGURE 27
(From Reference 123).

of the space between the electrodes, and region D represents the long-time conductance after the 'clean-up' of the oil by the current." The length of the various periods is strongly dependent on the voltage applied, increasing with decreasing voltage, at least down to the constant minimum conductance of the system. Oncley and Hollibaugh have shown that conductance data obtained over a wide range of voltage gradients could be represented on a single curve if they are plotted vs. volt × time. (Figure 27.) The ions which are responsible for the time-dependent conductivity are probably produced by ultraviolet radiation and the ever-present space radiation show-

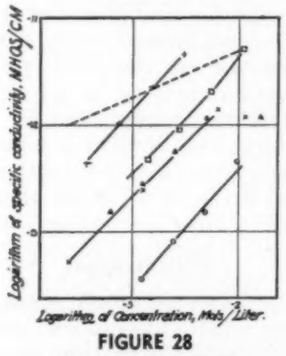

FIGURE 28
(From Reference 127).

ers. Exposure of lubricating oils to corona discharges or bombardment with alpha particles[124, 125] increases the d-c conductivity very considerably, also most likely due to the production of ions. The oxidation of transformer and other lubricating oils is not only accompanied by a large increase of the power factor, discussed in the previous paragraph, but also by a corresponding increase in electric conductivity. In many cases a large fraction of or almost the entire increase in power factor could be ascribed to the electric conductance, Table 35. Model experiments with solutions of various salts of organic acids and bases in mineral oil[126] showed that these substances increase the conductivity of the system more than the respective organic acids and bases alone. The

TABLE 35
Electrical Conductivity of Lubricating Oil Systems (All at 80° C.)

SYSTEM	d-c Conductivity at ~1 KV/cm 1 Min. 10^{-14} mhos/cm³	a-c Conductivity* at ~20 KV/cm 60 Cycles 10^{-14} mhos/cm³	Ref.
White Oil (61.6 cst/40° C.)	0.3	1.5	(126)
Same + 2.4 percent Piperidine	2.5	3.6	(126)
Same + 4.0 percent Piperidine Laurate	114	93	(126)
Same + 0.24 percent Lauryl Sulphonic Acid	143	191	(126)
Same + 6.0 percent n-Heptylmercaptan	4.8	19.3	(126)
Same + .06 percent Pb-1,10 Hydroxy stearate	40 (140)†	200 (369)†	(121)
Same + .25 percent Cu- " "	5 (45)†	7 (70)†	(121)
Same + 1.26 percent Polyisobutylene (M-10,000)	4.94	8.8	(124)
Cable Oil (new → bombarded)	2.5 → 17.7	12.3 → 313	(125)
Transformer Oil (new → used)	.....	7 → 560	(119)

* Calculated from: Power Factor x 7.3 x 10^{-11}.
† Values in parentheses are maxima at or near gel (cloud point) of system.

peculiarity of heterogeneous (colloidal, gel) systems exhibiting extreme values of power factors was also observed for the d-c conductivities. The latter were in most cases of the same order of magnitude as the equivalent conductivities calculated from power factors. Piper and co-workers advance the hypothesis that these phenomena should be ascribed to preferred dissociation of the salts present at the interface of the oil phase and the gel particles. The mechanism of conductance in oils and other liquids of low dielectric constant has been discussed by Gemant.[127] These very careful investigations demonstrated that the dissociation constant of relatively "strong" acids such as toluene sulfonic, lauryl sulfonic, and picric acids in such solvents was of the order $K \sim 10^{-20}$-10^{-22} and of weak acids resulting from oil oxidation, phenols and asphalt several orders of magnitude smaller yet. The hydrogen ion concentration is therefore by far too low to account for the observed conductivities. The direct proportionality between acid concentration and conductivity, Figure 28, suggests ion generation by reaction between certain cyclic hydrocarbon portions of a transformer oil and the organic acid: $R + HAc \rightleftharpoons RH^+ + Ac^-$.

Very considerable potentials have been observed between electrodes of different metals immersed in oxidized lubricating oils.[127a] The measured E.M.F. of such cells is quite temperature-dependent, reaching maximum values around 170° F. E.M.F. values of between 0.1 and 1.1 (!) volt have been observed in cells of cadmium-silver vs. steel, cadmium-silver vs. aluminum, and babbitt vs. steel in aged lube oil. The importance of such high potentials and more than negligible conductivity in oxidized and used lubricating oils for the phenomena of bearing corrosion is not always recognized (or appreciated).

IV.7 Dielectric Strength of Lubricating Oils

The dielectric strength of a lubricating oil is the maximum potential gradient in volt (or KV) per cm (or in ASTM Standards: KV/0.1 inch), which the oil will stand without permitting a visible and/or audible electrical discharge. Its absolute numerical value is a function of the shape of the electrodes and is at very small spark gaps not independent of the thickness of the exposed oil film. The result of dielectric-strength measurements is also very much affected by the rate of voltage or voltage gradient increase. Rapid increase often resulting in very much higher breakdown voltages than slow increase. Prolonged application of a relatively low potential gradient (as required by the British Specification BESA 148) may often be a more severe test than momentary high loads. This is probably due to two effects: (a) the

TABLE 36

Gas Evolution from Various Oils and Hydrocarbons Under the Influence of Corona Discharges (@ 15 KV, 50 KV/cm 60 cycles/sec. for 4 hrs.) from Ref.[125]

OIL	Viscosity at 40° C. cst	Gas Evolved cm^3/cm^3 of Sample
Hexadecane	3.1	6
Hexadecane	2.7	2
Decalin	2.2	4
Me-Naphthalene	2.2	0.5
Synthetic Oil (M=944)	670	11.5
Highly Refined Cable Oil	.....	11.0
Naphthenic Cable Oil	.....	2.0

slow rate of formation of "bridges" of impurities such as lint, moisture droplets or other foreign matter between the electrodes along which the discharge will ultimately take place, and (b) in very pure oils due to the slow rate of electron escape and consequent ionization of many of the oil molecules by cold cathode emission from the electrodes.[129,130] While the mechanism of the phenomena involved is not yet well understood one thing seems well established: that the dielectric strength is not dependent on the chemical composition of lubricating oils,[131] but is essentially a function of their freedom from foreign matter and moisture. Commercial lubricating-oil samples have been observed to show dielectric strengths of between 60 and 150 KV/cm, transformer oils should always be higher than 120 KV/cm (30 KV per 0.1 inch). The reviewer has tested many well refined transformer oils which carried voltage gradients of 380 KV . cm for more than 10 minutes. One will generally find the results (which in bad cases scatter wildly) to increase with the number of tests performed on a sample.

IV.8 The Electro-Chemistry of Lubricating Oils

The chemical changes of lubricating oils in the electrical field are so closely related to the phenomena treated in the previous paragraphs that it is preferred to describe them in this section rather than in the Section VII dealing with the chemical reactivity of lubricating oils.

When lubricating oils are for prolonged periods of time exposed to high alternating voltage stresses (4 KV and above) a number of physical and chemical changes are observed to occur. Gas bubbles appear within the liquid in a continuous stream, which at 15 KV and about 60 KV/cm gradient and sometimes even at lower voltages convert almost the entire mass of liquid into a froth. The composition of this gas has been determined by various investigators.[124,125] It consists mainly of hydrogen and methane, and to some extent of the C_2 to C_4 hydrocarbons. In a few cases carbon monoxide also was observed. The composition of the lubricating oil affects the amount of gas produced very decidedly.

TABLE 37

Inhibition of Gas Evolution by Additives (@ 7500 cycles, 25mA) from Ref.[133]

OIL	Duration of Test (Min.)	Pressure Increase (mm Hg)
Hexadecane	30	30
Cable Oil (Solvent Refined)	30	4
Cable Oil (Over-Refined)	30	15
USP—White Oil	30	13
USP—White Oil	50	20
Same + 2 percent Benzine	50	5
Same + 3 percent Xylene	50	4
Same + 2 percent Naphthalene	50	3
Same + 3.0 percent Tetralin	50	0
Same + 1.0 percent Aniline	48	2
Same + 1.0 percent Chinoline	48	0

The higher the content of hydrogen-rich (saturated) hydrocarbons and the lower the concentration of aromatics the more gas is evolved during this exposure to the electrical field, usually to the so-called corona-discharges. (Table 36.) This is in agreement with the findings of Schoepfle and Fellows[132] on pure hydrocarbons under the action of cathode rays and α — radiation. The influence of chemical composition on gas evolution from lubricating oils under the action of alternating electrical stresses has been most strikingly demonstrated by Nederbragt's[133] experiments. This author showed that addition of very small amounts of aromatic compounds may substantially reduce or even completely inhibit gas evolution. (Table 37.)

Concurrently with gas evolution one observes a steady increase of viscosity of the bombarded oil, and after some time solids start to precipitate until finally all the liquid seems transformed into a wax-like mass. This end product is commonly known as X-wax or cable cheese,[134,135,136] indicating its most frequent locale of occurrence. Such changes are obviously brought about by polymerization of those compounds which have been dehydrogenated by the electron (or ion) bombardment.[137,138] The products of polymerization are as a rule unsaturated hydrocarbons of polymerization degrees between 3 and 20 with increasing molecular weight. They become progressively more insoluble in the oil, indicating that the polymers formed are not linear but clustered. They impart strong increases in electrical conductivity to the oils in which they are dispersed[126] as has been mentioned above.

Both the evolution of gases and the deposition of solids is most undesirable in cable oils, aside from the incidental increase in electric loss due to power factor and conductivity rise. The refining of mineral oils for Pirelli and similar oil-filled cables and impregnants has therefore to be guided in such a manner that the percentage of aromatics left in the oil is large enough to inhibit gas evolution and wax formation but not so large as to seriously affect the oxidation resistance of the final product. Use of inhibitors for either purpose is not advised because of their probable rapid depletion by adsorption on the relatively large surfaces with which the oil is in contact and their adverse effect on the dielectric loss factor in solution as well as in the adsorbed (or absorbed) state.

Voltolization

The very process of polymerization by silent electrical discharge which has above been pictured as rather undesirable when occurring in cable oils can be of great utility when applied to the production (or better conversion) of excellent automotive lubricants under controlled conditions. This process of "voltolization" which was invented by de Hemptinne (in Belgium),[139] employs electrodes located in the center of a cylindrical tank between which oil is circulated as a thin film. The tank contains a hydrogen atmosphere of lower than atmospheric pressure. The potentials across the electrodes are around 4 to 10 KV. The frequency used is said to be around 500 to 1000 cycles. The current consumption is quite considerable, about 1 to 5 KWh per pound. The process is usually started by introducing a mixture 2:1 to 1:2 of rape-seed oil and refined mineral lubricating oil into the reactor. After the reaction is already well under way lubricating oil is slowly added until the

TABLE 38

Fractionation of Voltolised Oils with M.E.K. Ref.[140])

Oil No. 1 Temp.	Percent Precipitate	Sap. Number	Iodine N.	M ' Wt.	REMARKS
+20° C	7.8	135	..	....	Rubbery, red
+10	3.9	131	..	....	Stringy liq.
± 0	0.8	153	55	....	Salve, yellow
—10	8.6	130	47	2109	Salve, yellow
—20	7.2	133	42	1786	Salve ,yellow
—30	11.3	109	45	1224	Salve, yellow
—40	10.5	79	34	855	Viscous, yellow
—50	10.5	31	22	552	Fluid
—60	8.6	31	22	516	Fluid
Soluble	31.3	13.2	33 !	419	Vis. at 50° C= 107cst. V-I=22

Oil No.2 Temp.	Percent Precipitate	Neu. No.	Sap. Number	Iodine N	M ' Wt.	REMARKS
—	100	2.4	164	74.8	1628	Liq. reddish yel.
—10	17	1.6	165.7	70	....	
—20	14	1.57	164.6	....	....	
—30	17.8	2.08	164.6	....	2293	
—40	12.8	2.02	167	....	1900	
—50	17.2	2.01	167	....	1433	
—60	10	3.22	169	76.3	1416	
Soluble	11.2	13.8 !	134.5	80.2	724	
Oil No. 3:						
0° C	41.4	1.34	74.1	....	....	
—20	12.3	1.05	79.3	....	....	
—30	4.6	2.5	53.7	....	....	
Soluble	40.2	1.28	15.9	....	....	Vis. at 50° C= 162 cst V-I= 85
Oil No. 4:						
+20° C	32	....	2.8	....	779	
Soluble	68	....	1.8	....	516	Vis. at 50° C= 152 cst. V-I= 68

finished batch contains 5 to 15 percent of rape-seed oil. Lubricating oils can also be voltolized by themselves, but the resulting product does not show, as a rule, as well improved viscosity-index as the compounded oils. The composition of voltols and the reaction mechanism have been studied with the help of low-temperature methyl-ethyl-ketone (MEK) fractionation.[140] The polymerization products are insoluble in cold MEK while the oil stays in solution even at low temperatures (?). In Table 38 some typical results of such fractionation are assembled. The oil No. 1 was prepared by voltolizing 33 parts of rape-seed oil to a viscosity of 68 cst at 100° C, then adding stepwise 67 parts petroleum lubricating oil while voltolizing to a viscosity of 190 cst at 100° C. The saponification number of the polymer fractions indicates that out of every four molecules taking part in polymerization (or condensation) reactions, only one is a lubricating-oil hydrocarbon under the condition employed. Oil No. 2 is straight rape-seed oil voltolized to a viscosity of 69 cst at 100° C. The measured molecular weights of the polymer fractions are of the same order as those of oil No. 1. But the saponification numbers are quite high, indicating that the ester bond stays unaffected by the polymerization reaction. It is, indeed, interesting to observe that the free fatty acids are enriched in the unpolymerized fraction. Oil No. 3 was prepared by voltolizing a blend of ⅓ rape-seed oil and ⅔ petroleum lubricating oil. The low saponification number of the polymer fraction indicates that out of each 3 molecules combining in the polymerization reaction, 1 was a rape-seed molecule while 2 were supplied by the lubricating oil. The high iodine number of the unpolymerized hydrocarbon fraction is quite remarkable (only 6 units could possibly be due to the saponifiable component). Only a preliminary test fractionation of a voltolized straight mineral oil had been included in these data. Petrov[141] has voltolized various hydrocarbon materials and found that aromatic hydrocarbons yield oils of low viscosity index while paraffines yield oils of high V.I. This closely parallels common experience with aluminum chloride catalyzed polymerization of thermally dehydrogenated (slightly cracked) petroleum fractions, where also the aromatic fractions are found to give low V.I. polymer oils while paraffin wax produces oils of 120 to 150 V.I. This similarity is not at all surprising if we remember that modern theory of the aluminum chloride catalyzed hydrocarbon reactions assumes the activated state to also involve the carbonium ion.[142]

The popularity of the voltols in European countries was originally due to their high V.I. and good oxidation stability. These properties alone did not suffice to make them competitive with solvent-refined or natural paraffinic oils on the American market. During the past few years it has been found, however, that voltols compare in detergency properties very favorably with additive-loaded heavy-duty motor oils. In view of the premium which these oils command it appears probable that voltols may enter the domestic market as heavy-duty motor oils. Whoever will embark into this interesting field is due, however, for some stiff development problems since the know-how of the process has been held as closely-guarded secret by its owners.

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Streamlined Orifice Calculations

E. E. McREYNOLDS

THE following outline for orifice calculations is a simplified method for accurate calculations in which the effects of the fundamental variables can be seen at a glance. One of its features is the elimination of two-way tabular interpolation which is necessary when using tables of discharge coefficients or when using the tables of various "correction factors" which are used in other methods. Supplied with the outline are charts for the discharge coefficient at infinite Reynolds Number; the Reynolds Number correction factor, F_{Re}, defined by $K = K_\infty F_{Re}$ where $F_{Re} = 1 + \frac{A}{Re}$; the expansion factor for gases and vapors, Y; and the factor, α, for correcting for the thermal expansion of the orifice at high or low temperatures.

For detailed information on the theory and practice of orifice meter installation and operation, the reader is referred to the reports of the Joint Committee on Orifice Coefficients of the American Gas Association and the American Society of Mechanical Engineers, and to "Principles and Practice of Flow Meter Engineering," by L. K. Spink, published by The Foxboro Company.

The deleterious effect on accurate flow measurement of improper meter installation is undoubtedly a more expensive item in industry than generally supposed, since the value of test data on a plant is usually dependant to a considerable degree upon the accuracy of flow measurement. Much time and money is spent in technical trouble-shooting which could be saved by installing meters as properly as reasonably possible instead of merely for the purpose of "operating indications." With reasonable care in ordinary industrial installations, the minimum probable error in orifice flow measurement is about plus or minus one percent.

Flow Calculations for Orifice Meters with Flange Taps

I. Steps in Calculating Flows.

1. Fluid: Definition	Term	Source
(a) Actual inside pipe diameter	D_1	---
(b) Orifice diameter	D_2	---
(c) Ratio of orifice diameter to pipe inside diameter	β	D_2/D_1
(d) Discharge Coefficient at Infinite Reynolds Number	K_∞	Fig.IA,B,C.
(e) Range tube size, Dry (ie., h_w at full scale)	R	---
(f) Orifice area multiplier for orifice temperature	α	Fig. III
(g) Integrated average flow pen reading on L-10 chart	L_1	Chart
(h) Specific gravity of mercury at manometer temperature	G_m	Lit.
(i) Specific gravity of seal fluid at seal line temp. (ref H_2O)	G_s	Lit.
(j) Absolute viscosity of flowing fluid, centipoises	z	Lit.
(k) For calculating pounds per hour of any fluid, density of fluid at upstream of orifice conditions	P_1	Lit.
(l) For gases or vapors; Molecular Weight,	M	---
Ratio of Specific Heats at orifice conditions,	k	Lit.
Orifice Pressure Drop, psi. $= P_1 - P_2 = \Delta P =$		$\frac{L_1^2 R(G_m - G_s)}{1357}$
Orifice expansion factor	Y	Fig. IV
Upstream of orifice temperature, °R = °F + 460	T_1	---
Upstream of orifice pressure, pounds per sq. in. abs.	P_1	---
Compressibility factor at flowing conditions	μ_1	Lit.
For converting pounds per hour to standard cu. ft., compressibility factor at standard conditions	μ_{60}	Lit.
(m) For liquids; Flowing specific gravity ref. H_2O @ 60° F	G_f	Lit.
For converting pounds per hour of liquids to standard volume units, specific gravity at 1 atm. & 60°	G_{60}	Lit.

2. Depending on the units desired, evaluate the bracketed term in one of the following equations:

(a) For any fluid; (Y for liquids is 1.0000)

$$W = \left[9.75\,(D_2)^2 \alpha \sqrt{R(G_m - G_s)}\ \ (K_\infty)\ Y\ L_1 \sqrt{\rho 1} \right] F_{Re} \quad ; \text{ W in lbs./hour.}$$

(b) For Liquids;

$$W = \left[77.00\,(D_2)^2 \alpha \sqrt{R(G_m - G_s)}\ \ (K_\infty)\ L_1 \sqrt{G_f} \right] F_{Re}; \text{ W in lbs./hour.}$$

$$\text{G.P.H.} = \left[9.24\,(D_2)^2 \alpha \sqrt{R(G_m - G_s)}\ \ (K_\infty)\ \frac{L_1}{G_{60}}\ \sqrt{G_f} \right] F_{Re}$$

(c) For Gases or Vapors;

$$W = \left[2.975\,(D_2)^2 \alpha \sqrt{R(G_m - G_s)}\ \ (K_\infty)\ Y\ L_1 \sqrt{\frac{M\,P_1}{T_1\,\mu_1}} \right] F_{Re}; \text{ W in lbs./hour.}$$

$$\text{S.C.F.H.} = \left[1130\,(D_2)^2 \alpha \sqrt{R(G_m - G_s)}\ \ (K_\infty)\ Y\ L_1\,\mu_{60} \sqrt{\frac{P_1}{M\,T_1\,\mu_1}} \right] F_{Re}$$

3. The bracketed part of the above equations is the flow if the Reynolds Number is infinite. Using a value of W from step 2 equal to the term in brackets, calculate the Reynolds Number from the formula,

$$Re_a = \frac{6.31\,W}{D_2\,z}$$

Using Figure II, following the horizontal line determined by β and the pipe size (lines of constant "A"), read F_{Re} corresponding to the above Reynolds Number.

Multiply Re_a by the above F_{Re} to obtain the corrected Reynolds Number. Then read a new value of F_{Re} at the corrected Reynolds Number. Multiply the original value of the Reynolds Number, Re_a, by the newer, more nearly correct F_{Re} each time, thus obtaining a more nearly correct Reynolds Number each time. Continue this process until successive values of F_{Re} are the same.

For example, suppose $\beta = 0.6050$, $D_1 = 10.136$, and step 3 gives $Re_a = 46{,}000$. From Figure II, $F_{Re} = 1.050$. Therefore, Re must be nearer $46{,}000 \times 1.050 = 48{,}300$. For Re of 48,300, (on the same horizontal "A" line), F_{Re} is 1.0475. Using the original uncorrected Re_a each time, we have $1.0475 \times 46{,}000 = 48{,}180$. Since no difference in F_{Re} can be read on the chart at a Reynolds Number of 48,180, any further refinement in the value of F_{Re} is not necessary, and the correct value is 1.0475.

4. Having obtained the correct value of F_{Re}, calculate the corrected flow.

5. For unit meter factors, divide the result of step 4 by L_1. For accurate calculations, it is necessary to plot any normal variables (such as Re) which may change the unit factor, each versus a correction factor which may be applied to the daily calculations.

[*Text continued on page 135*]

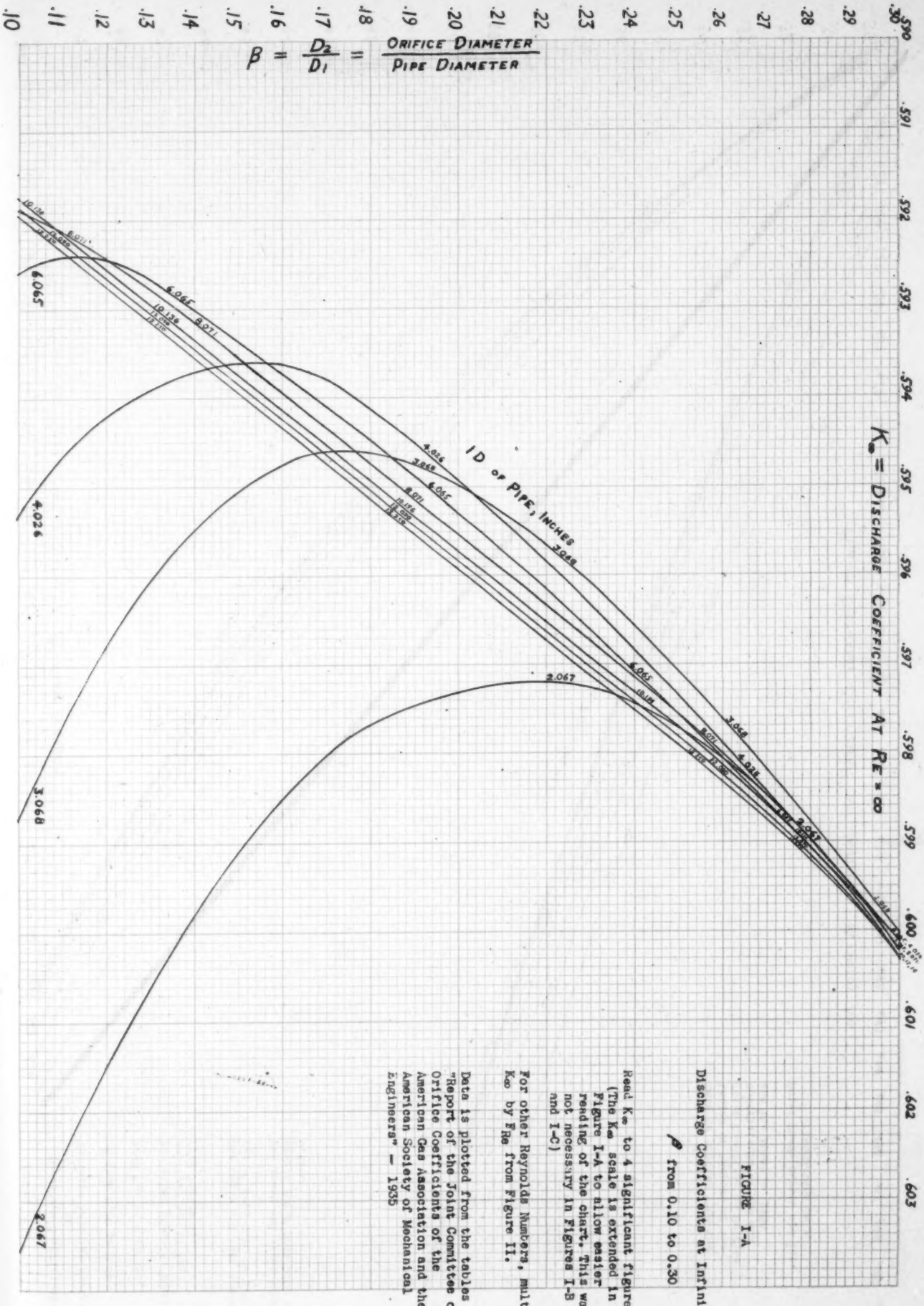


FIGURE I-A

Discharge Coefficients at Infinite Re.

β from 0.10 to 0.30

Read K_∞ to 4 significant figures. (The K_∞ scale is extended in Figure I-A to allow easier reading of the chart. This was not necessary in Figures I-B and I-C)

For other Reynolds Numbers, multiply K_∞ by Re from Figure II.

Data is plotted from the tables of "Report of the Joint Committee on Orifice Coefficients of the American Gas Association and the American Society of Mechanical Engineers" — 1935

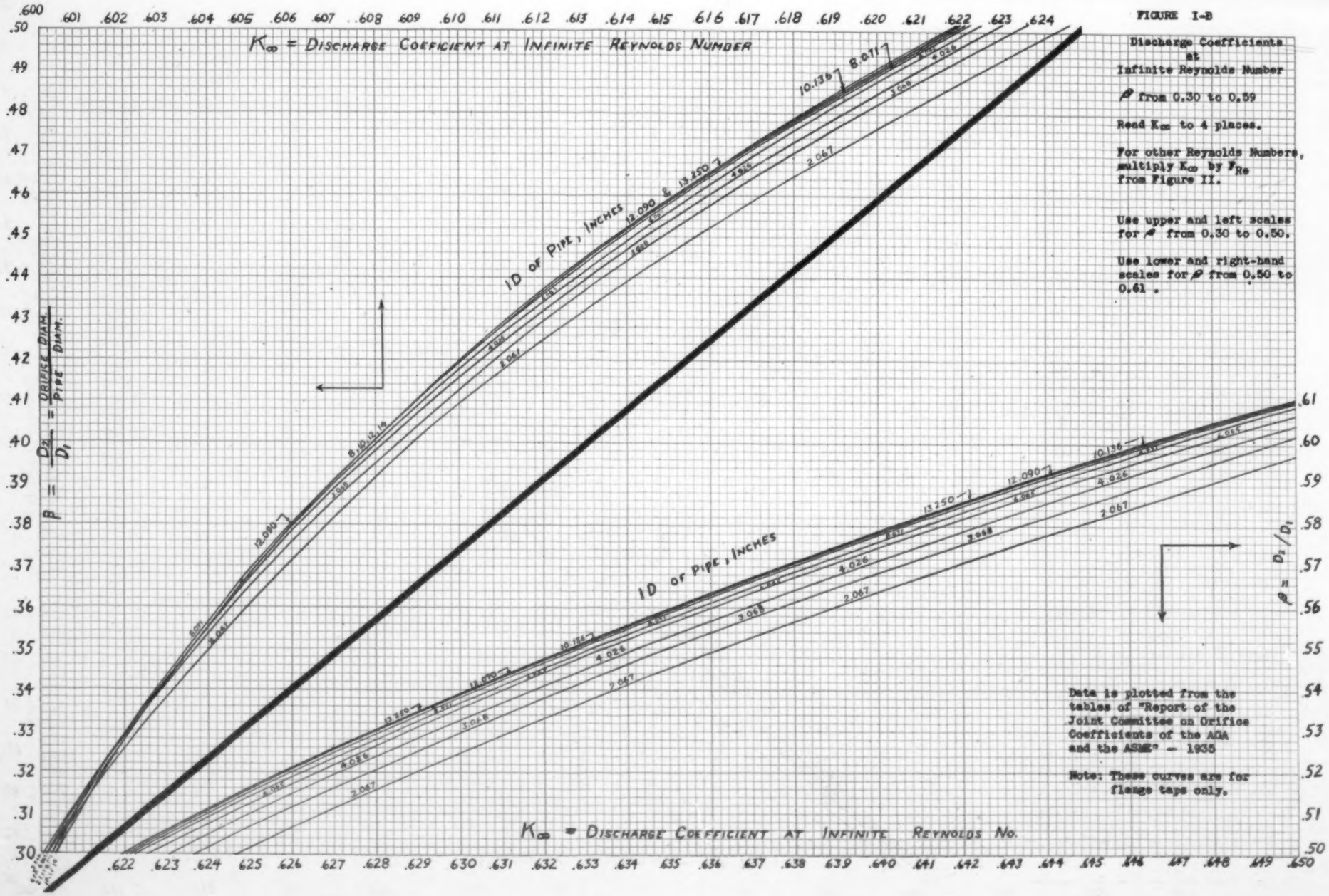


FIGURE I-B

Discharge Coefficients at Infinite Reynolds Number

β from 0.30 to 0.59

Read K_∞ to 4 places.

For other Reynolds Numbers, multiply K_∞ by F_{Re} from Figure II.

Use upper and left scales for β from 0.30 to 0.50.

Use lower and right-hand scales for β from 0.50 to 0.61.

Data is plotted from the tables of "Report of the Joint Committee on Orifice Coefficients of the AGA and the ASME" — 1935

Note: These curves are for flange taps only.

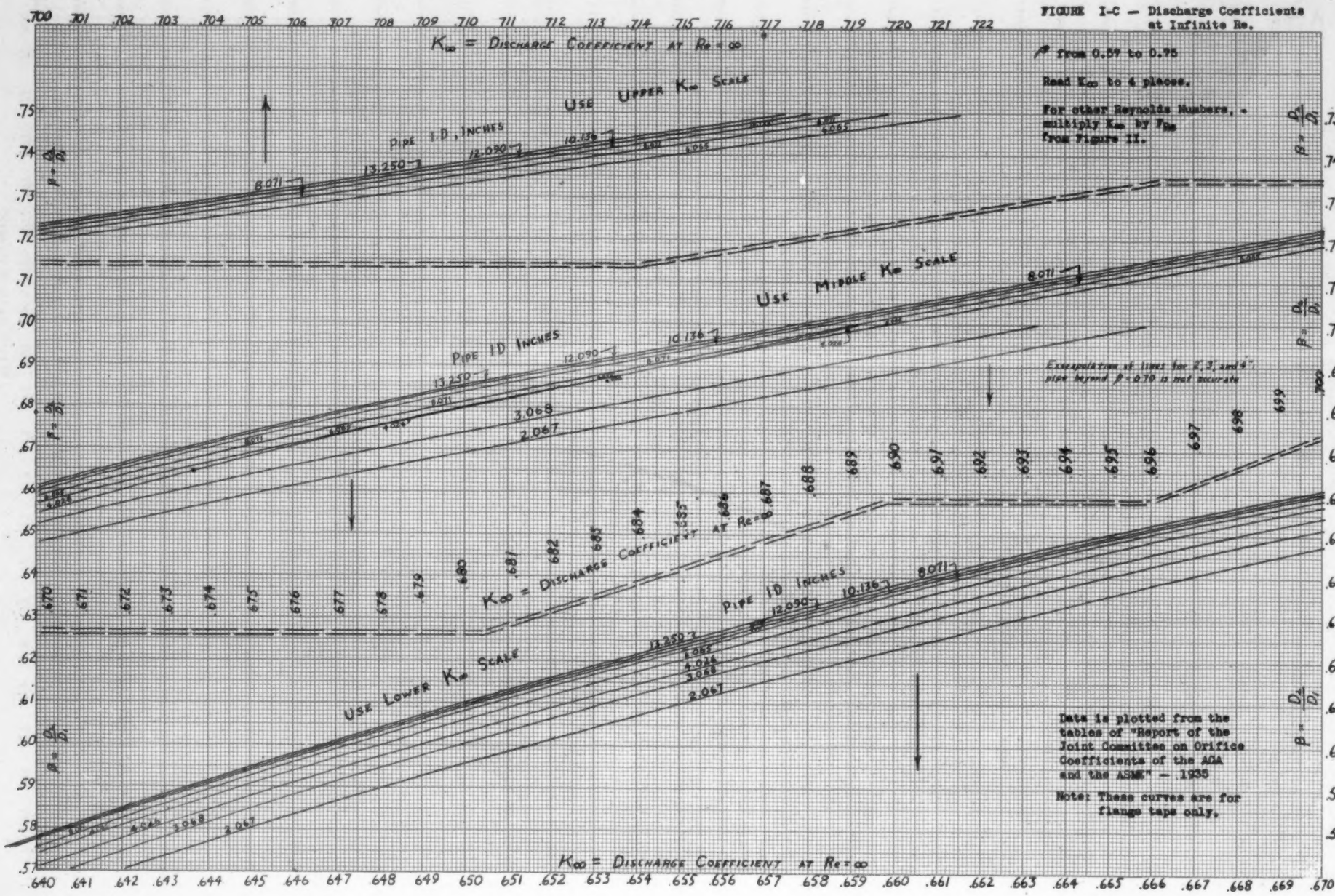

K_∞ = Discharge Coefficient at Re = ∞
Use Upper K_∞ Scale
Use Middle K_∞ Scale
Use Lower K_∞ Scale
Pipe I.D., Inches
Pipe ID Inches
13.250
12.090
10.136
8.071
6.065
5.047
4.026
3.068
2.067
$\beta = \frac{D_2}{D_1}$
Extrapolation of lines for 2, 3, and 4" pipe beyond β = 0.70 is not accurate
Data is plotted from the tables of "Report of the Joint Committee on Orifice Coefficients of the ASA and the ASME" — 1935
Note: These curves are for flange taps only.
K_∞ = Discharge Coefficient at Re = ∞

FIGURE I-C — Discharge Coefficients at Infinite Re.

β from 0.59 to 0.75

Read K_∞ to 4 places.

For other Reynolds Numbers, multiply K_∞ by F_{Re} from Figure II.

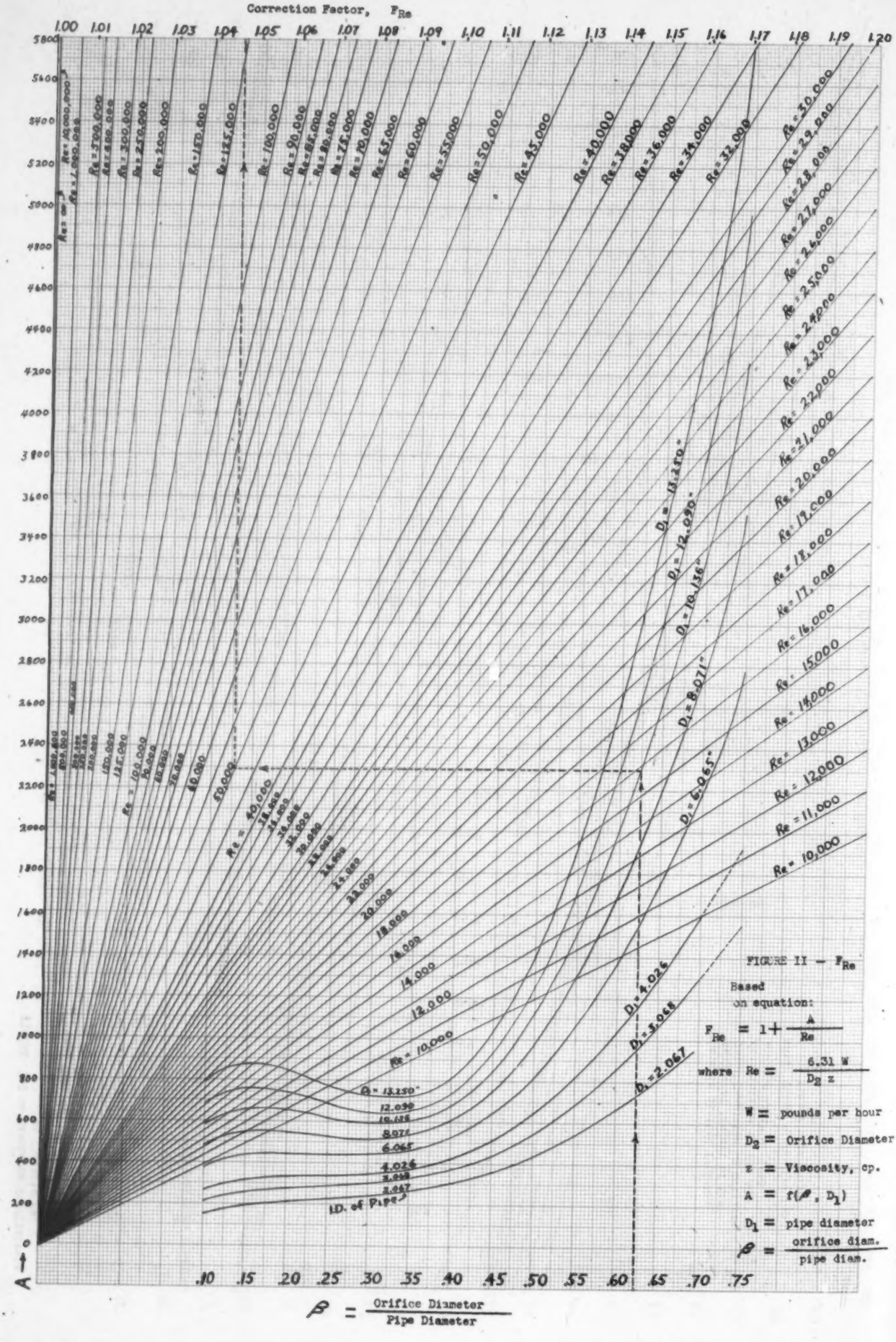


FIGURE II – F_{Re}

Based on equation:

$$F_{Re} = 1 + \frac{A}{Re}$$

where $Re = \frac{6.31\ W}{D_2\ z}$

W = pounds per hour

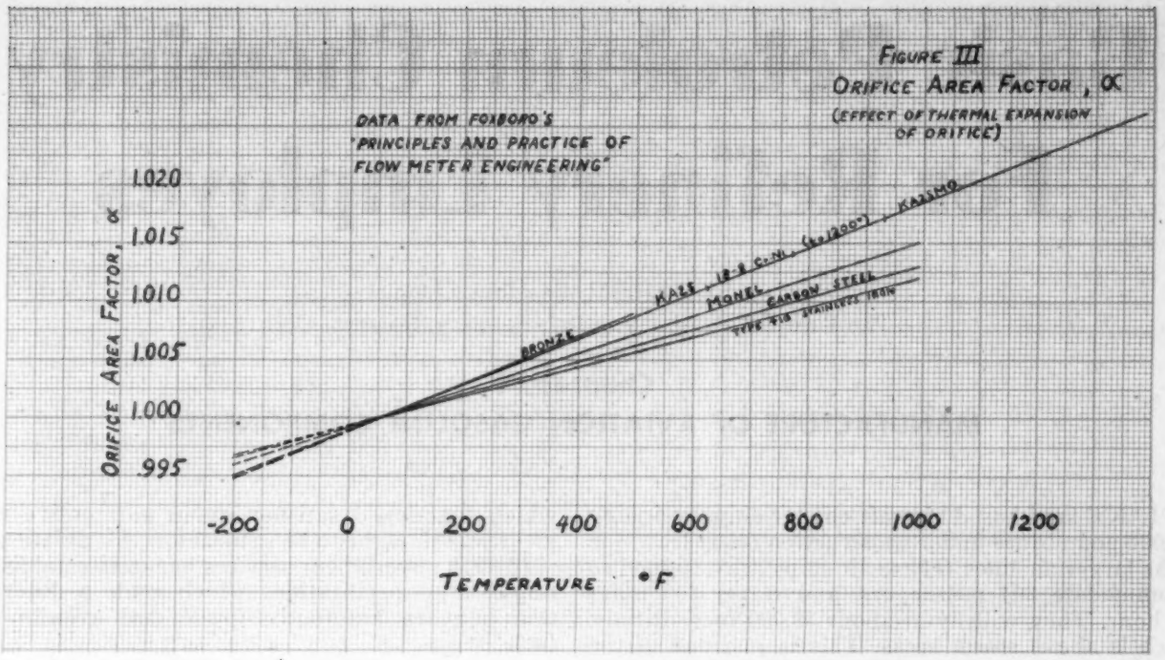
D_2 = Orifice Diameter

z = Viscosity, cp.

A = $f(\beta, D_1)$

D_1 = pipe diameter

β = orifice diam. / pipe diam.



II. Sources of Material

1. *Equations*

From the equation

$$w' = 0.525\, K Y D_2^2 \sqrt{\rho_1\ (P_1 - P_2)}$$

from "Report of the Joint Committee on Orifice Coefficients of the American Gas Association and the American Society of Mechanical Engineers," 1935, where $w' =$ mass rate of flow, pounds/second and the other symbols are as defined in section I; substituting

$$0.3613\, h_w = P_1 - P_2 \quad \text{and}$$

$$h_w = \left(\frac{L}{10}\right)^2 \frac{(G_m - G_a)}{G_m @ 60°F} R \quad ;$$

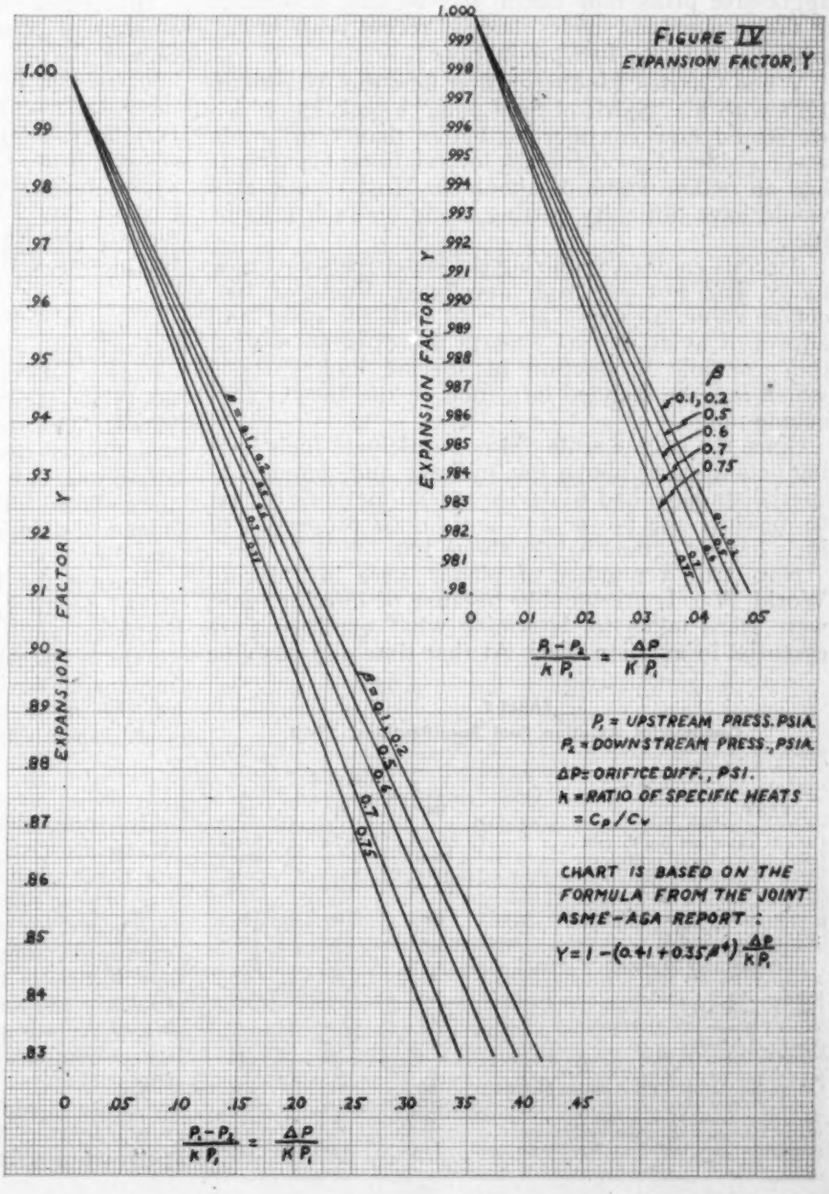
substituting $L_1 =$ integrated average L; substituting $W = 3660\ w'$; introducing the factor, α, the correction for thermal expansion of the orifice and substituting $K \propto F_{Re} = K$; is obtained the expression,

$$W = \left[\ 9.75\,(D_2)^2 \alpha \sqrt{R(G_m - G_a)}\ (K_\infty)\ Y\ L_1 \sqrt{\rho_1}\ \right] F_{Re}$$

pounds per hour. From this equation, the other equations of Section I are easily derived. For meters not using direct-reading L-10 charts, the appropriate changes in the flow equations can easily be made.

2. *Charts*

The feature of this paper is the correlation of the Discharge Coefficients at any Reynolds Number with the Discharge Coefficients at Infinite Reynolds Number in Figures I and II. Use of these charts eliminates the necessity of interpolation in tables of discharge coefficients, thus saving time and gaining in accuracy. The F_{Re} factor chart can also be used in conjunction with other meter calculation methods. The other charts are self-explanatory.



Basic Petroleum Chemistry For Refinery Employes

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Chapter VI

MANUFACTURE OF AVIATION GASOLINE COMPONENTS

GIANT land-based aircraft clipper ships weighing 320,000 pounds are under construction for at least one of the larger air lines. These air ships are designed to accommodate 204 passengers, and travel 300 miles per hour. They will fly at about 30,000 feet altitude, which is above storm areas. This is just one of the aggressive plans now under way to take advantage of the tremendous strides made in recent years in aircraft and aviation-fuel production.

When Charles Lindbergh first flew the Atlantic in 1927 with his "Spirit of St. Louis," a gasoline which we would now consider no better than third-grade was considered good enough for aviation purposes. It had an octane value of about 60. Most of our cars would have difficulty getting along on such inferior fuel.

Aircraft engines, requiring the super fuels we know today, had not yet been developed. Fuels of 100-octane value are now considered none too good, and efforts of aviation fuel experts are directed toward the economic production of specific hydrocarbons which may be blended into fuels in the 130- to 150-octane range.

Since the octane scale did not anticipate fuels having octane value above 100, military and commercial specialists have had to devise special methods of test to measure the power and anti-knock properties of fuels having octane values above 100.

Not until a number of planes were lost during World War I, presumably because of inferior fuels, were steps taken to determine what qualities were essential in aviation fuels. At that time any gasoline which functioned satisfactory in automotive equipment was thought to be satisfactory for aviation fuel.

In 1918 government services began to establish distinguishing specifications which made a differentiation between automotive-grade and aviation-grade fuel.

Investigations conducted by the United States Bureau of Mines and the Aviation Section of the Signal Corps, indicated that blends of 30 percent benzene and 70 percent cyclohexane seemed to be the most satisfactory fuel for fighting aircraft of that period. Closely fractionated cuts out of selected crudes from California, South Texas, and Venezuela—blends of straight-run gasoline benzene and alcohol—and blends of straight-run gasoline and natural gasoline were found to be suitable fuels for the planes of the 1917-to-1927 period.

Cracked Gasoline in Aviation Fuel

During this period (1917-1927) cracking processes experienced extensive development, and some cracked materials were beginning to be used in aviation blends. The quantity which it was possible to use was limited because of a specification which did not allow over 1.0 percent unsaturated hydrocarbons in the finished blend. This specification was later abandoned and in its place was substituted an oxygen-stability test.

During the 1917-1927 period, research had established definitely the relationship between engine performance and fuel knocking characteristics.[1] This led to the adaptation of the octane scale as a standard measuring device. The octane value then became one of the most important specifications for internal-combustion engine fuels.

Specifications

In June, 1941, the American Society for Testing Materials (ASTM) accepted tentative specifications for three grades of aviation gasoline for commercial use. These specifications are listed in Table 7.

Except for the octane value, the tetraethyl lead maximum allowable, and the net calorific value, the specifications for these three grades of commercial fuel are the same. The specifications for Army and Navy Aviation Fuels (not available for publication) were comparable to the higher-octane commercial fuels.

These specifications had been established after much testing and research on the part of aviation and petroleum-refining experts. Each test is significant in

TABLE 7
Commercial Aviation Fuel Specifications, 1942

TEST	GRADE 100	91	73
Calorific value, net Btu lb. min.	18,700	18,700	18,300
Color	Blue	Blue	Blue
Corrosion, Copper Dish	None	None	None
Corrosion, Copper Strip	None	None	None
Distillation:			
10 Percent °F. Max.	158	158	158
50 Percent °F. Max.	212	212	212
90 Percent °F. Max.	257	257	257
10 Percent plus 50 percnet °F. Min.	307	307	307
Recovery, Percent Min.	97	97	97
Residue, Percent Max.	1.5	1.5	1.5
Loss, Percent Max.	1.5	1.5	1.5
Vapor Pressure, lbs. Max.	7.0	7.0	7.0
Acidity of Residue	None	None	None
Freezing Point, °F. Max.	—76	—76	—76
Gum, accelerated, Mg./100cc Max.	6	6	6
Octane No. ASTM-CFR Aviation Method	100	91	73
Sulfur, Percent Max.	0.05	0.05	0.05
Tetraethyl Lead, Max. cc/gal.	3	4	1
Water Tolerance, Max. volume change ±	2	2	2
Permissible gum inhibitors, lbs./500 gal.	1.0	1.0	1.0

the overall quality of the finished product. Consequently there are relatively few hydrocarbons which alone would function as a suitable aviation fuel. The hydrocarbons must be blended together to arrive at the desirable characteristics. Benzene for instance, while it has a high octane value, may be used in aviation blends to a very limited extent because of its high freezing point of 42° F. and low calorific value of 17,200 Btu per pound.

In order to get the combination of qualities which add up to make a suitable aviation fuel, five types of products are blended together. They are: (1) a base stock consisting of high-octane straight-run and/or special cuts taken out of straight-run, catalytic-cracked or natural gasolines, (2) a high-octane, high-lead-susceptibile blending agent consisting of such hydrocarbons as benzene, isooctanes, neohexane, xylines, cumene, cumene substitute, triptane and other high-octane hydrocarbons, (3) a hydrocarbon mixture containing such compounds as isopentane, neopentane and hydrocarbon cuts of similar volatility to impart the desired volatility to the blend, (4) tetraethyl lead to increase the power and octane value, and (5) oxidation inhibitors to retard the formation of gum in the blended fuel.

Base Stock

A suitable base stock for aviation blends has two purposes. It imparts to the final blend the required distillation range, and it expands the volume of aviation-grade fuel which may be blended from available materials. The latter is of course primarily an economic consideration. The high-octane components used in aviation blends usually have narrow boiling ranges, since in some instances the high-octane component is a single hydrocarbon containing only traces of contaminating substances. The contaminating compounds may be similar in chemical and physical properties to the chief constituent. The boiling range is seldom within the limits of a good aviation fuel, making a wider-boiling-range base stock necessary.

The base stock should have these characteristics:

(1) A smooth distillation curve which conforms to the specifications when blended with the other materials to go into the blend.
(2) Freedom from butane and lighter hydrocarbons.
(3) A very low freezing point.
(4) Stable to the formation of gum.
(5) Low sulfur content.
(6) High octane and good response to the addition of tetraethyl lead (lead susceptibility).

Base stock having these characteristics are available from certain crude oils. Straight-run cuts boiling between 100° F. and 300° F. from naphthenic and naphthenic-intermediate base crudes are satisfactory. A suitable base stock containing significant concentrations of isopentane may be recovered from selected natural gasolines.[2]

All of the catalytic processes discussed in Chapter V may be operated to yield good quality aviation base stocks.[3,4,5,6,7]

High-Octane Blending Agents

The chemical combination of two or more like molecules to form one of higher molecular weight and higher boiling point, without the loss of any of the atoms existing in the original compounds, is called *polymerization.* The charge to a polymerization process is referred to as the *monomer,* and the reaction product of two monomers is called the *dimer.* Polymerization processes in which only dimers are formed are sometimes referred to as *dimerization* processes. If three monomers enter into a reaction to form only one molecule, the molecule is called a *trimer.* The production from polymerization operations containing a combination of reaction products is called *polymer.* Since the charge to most polymer gasoline operations consists of a variety of unsaturated molecules which interpolymerize, the term *codimer* often is applied to the product.

The reaction of two similar unsaturated hydrocarbon molecules can be induced by both thermal and catalytic technique.

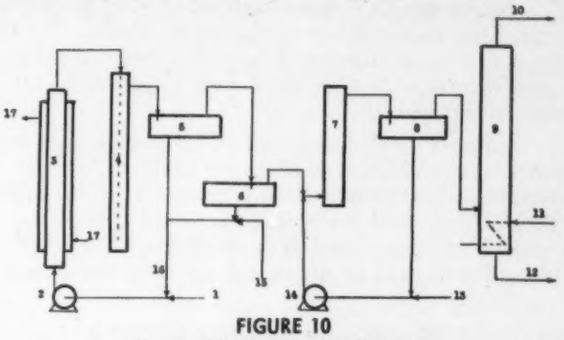


FIGURE 10

Hot Acid Polymerization Diagram

1 Charge; 2 Charge Pump; 3 Jacketed Reactor; 4 Reactor Time Tank; 5 Separator; 6 Acid Settler; 7 Caustic Scrubber; 8 Caustic Settler; 9 Fractionator; 10 Unreacted B.B.; 11 Steam Reboiler; 12 Polymer; 13 Fresh Caustic; 14 Caustic Pump; 15 Fresh Acid; 16 Recycle Acid; 17 Cooling Water.

Thermal polymerization of ethene, propene, butene and pentene when diluted with paraffin hydrocarbons, takes place at temperatures between 900° F. and 1100° F. and pressures between 1500 and 2000 psi.

Isooctene (2,2,4-trimethyl pentene) is a dimer of the dimerization of two molecules of isobutene. When the unsaturated bonds are satisfied by hydrogenation the corresponding isooctane is formed. In chemically pure form this hydrocarbon is a standard reference fuel for the determination of octane value, since by definition of octane value it has an arbitrarily assigned value of 100. There are 17 possible isooctanes, all of which may be expected to have good anti-knock properties. At least one of the 17 is known to have anti-knock properties superior to the well known 2,2,4 trimethyl pentane.[8]

When efforts are made to limit the composition of the charging stock to only certain molecules, butenes and isobutenes with butane diluent, the charge is referred to as "B.B." and the polymerization is said to be *selective.* When no effort is made to segregate specific molecules for polymerization, the process is called *nonselective.*

Three catalytic polymerization processes accounted for a sizable percentage of the high-octane components which went into the blending of over a half million barrels of aviation fuel per day during the final weeks of the war. Sulfuric acid was used as catalyst in two of the processes. One was known as the "hot-acid process" and the other as the "cold-acid process." The third process made use of phosphoric acid as the catalyst.

The cold-acid method provides for the contacting of the charge consisting of isobutenes with 60 to 70 percent sulfuric acid at 68 to 95° F. The mixture of acid and charge then passes through a coil heater held at about 212° F. The rate through the heater is such as to allow one minute contact time. The hydrocarbon layer is then separated from the acid layer, caustic washed, and distilled. Only the isobutenes react with these conditions of operation, and the product formed is mostly 2,2,4-trimethyl pentene.

The hot-acid method is a more recent development. Jacketed reactors are used to control the temperature

because the reaction is exothermic and requires cooling to prevent over-polymerization. Acid concentration is 63 to 72 percent H_2SO_4. The contact temperature is about 212° F. for the 63 percent acid and 167° F. for the 72 percent acid. Contact time in the time tank averages 10 to 15 minutes depending upon a number of variables such as the strength of the acid, temperature, concentration of olefins in the charge, and ratio of iso- to normal olefins. In this method not only isobutene but also normal butenes are polymerized. A simplified flow diagram is represented in Figure 10.

A number of both large and small plants were constructed rather hastily during an early period in our participation in the war to polymerize B.B. by means of the U.O.P. Solid Phosphoric Acid Process. See Figure 11 for simplified flow diagram. The catalyst of phosphoric acid is absorbed on clay and pressed into pellets.

As in the sulfuric acid methods the operating conditions depend upon the nature of the charge. Temperature of the heated gas into the reaction chamber is usually held between 290 and 350° F. The pressure is held between 500 and 800 psi, and the outlet of the reactor at about 450 to 500° F. The reacted material is debutanized and sent to storage. One percent water is introduced with the charge, and if two reactors are used, additional water is injected between the two reactors. If only one reactor is used additional water may be injected in the mid section of the single reactor. The water prevents the dehydration of the phosphoric acid catalyst which becomes inactive if allowed to dehydrate.

This process also may be used with modifications for the addition of light olefins to the benzene ring with the formation of high-octane compounds.

Below are some of the reactions which take place in the polymerization of light olefins:

The final product of each of the reactions illustrated above is an unsaturated molecule, and in order to be used to an advantage in aviation blends the double bond must be satisfied with hydrogen. Hydrogenation makes the product more stable to formation of gum, and increases the octane value.

Processes for the hydrogenation of unsaturated hydrocarbon molecules consist of equipment for contacting the hydrogen with the hydrocarbon at temperatures usually under 660° F., pressures varying from atmospheric to 3000 psi, and in the presence of a catalyst such as a compound of nickel, platinum, polladium, cobalt, molybdenum and tungsten.

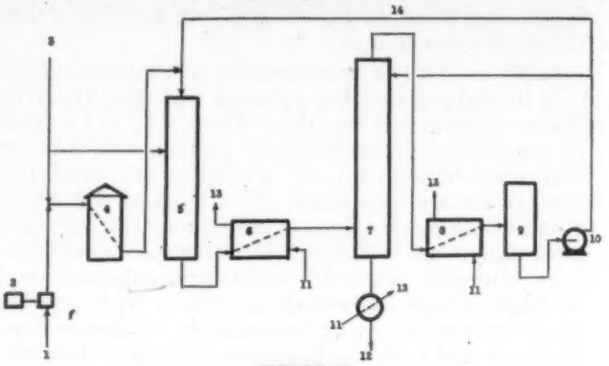
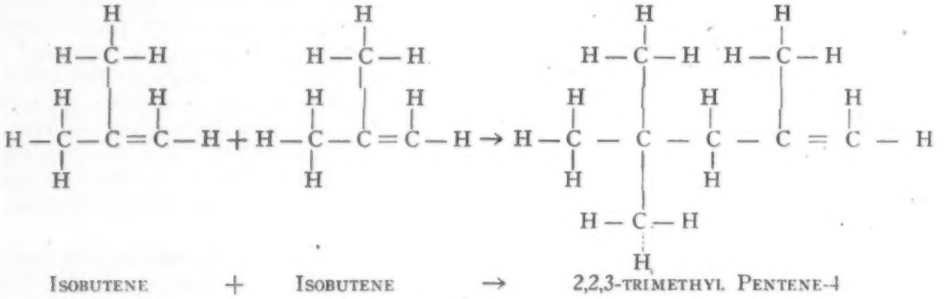


FIGURE 11
Phosphoric Acid Polymerization Process
1 Charge; 2 Charge Compressor; 3 Water; 4 Heater; 5 Catalyst Chamber; 6 Condenser; 7 Stabilizer; 8 Condenser; 9 Reflux Accumulator; 10 Reflux and Recycle Pump; 11 Water In; 12 Polymer; 13 Water Out; 14 Recycle.

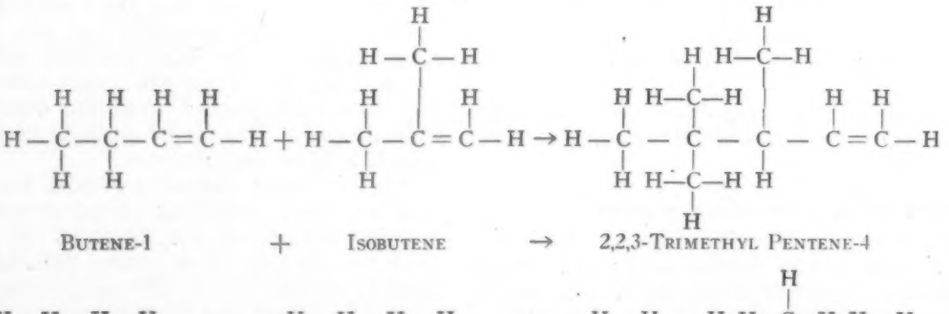
Alkylation

During the war the most important synthetic processes for making high octane blending agents were those known as *alkylation* processes. The high octane liquid from these processes is called *alkylate*.

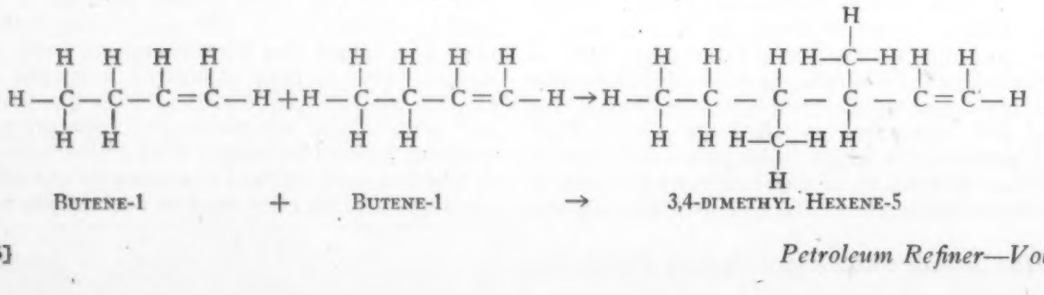
The chemical reaction in alkylation involves the joining of an alkyl group, that is CH_3, C_2H_5, C_3H_7,



ISOBUTENE + ISOBUTENE → 2,2,3-TRIMETHYL PENTENE-1

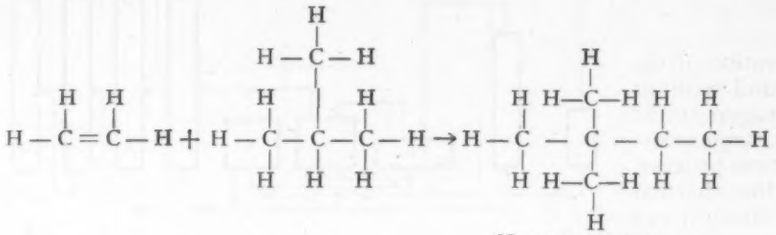


BUTENE-1 + ISOBUTENE → 2,2,3-TRIMETHYL PENTENE-1



BUTENE-1 + BUTENE-1 → 3,4-DIMETHYL HEXENE-5

etc., with another hydrocarbon compound. The alkyl group is substituted for a hydrogen atom on any hydrocarbon compound. The reaction may be induced by either thermal or catalytic methods. If induced by heat and pressure only, the process is said to be *thermal alkylation.* The Neohexane process is an example of thermal alkylation.[9] The reaction in the Neohexane process is represented as follows:



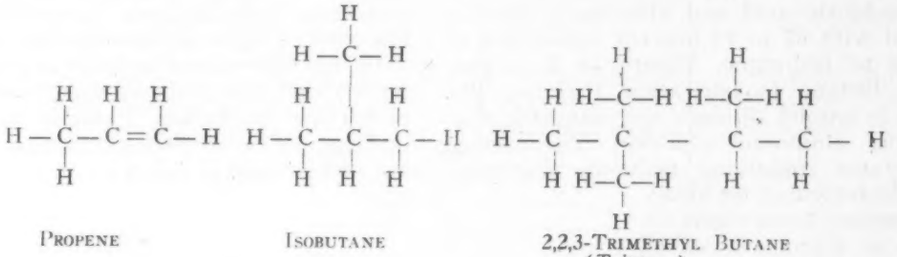
ETHENE + ISOBUTANE → NEOHEXANE OR 2,2-DIMETHYL BUTANE

Chlorides of aluminum, lithium, tin, tantalum, antimony, bromides of aluminum and tantalum, and oxides of tantalum titanium, silicon and vanadium have all been used as catalysts with some degree of success in alkylation reactions. Sulfurnic acid and hydrogen fluoride were used in the war for synthetic production of high-octane hydrocarbons.

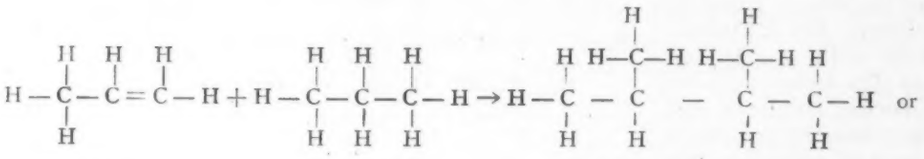
The sulfuric acid methods are so closely associated with sulfuric acid polymerization that the processes are often considered the same. The difference resides in the fact that sulfuric acid polymerization causes the joining of two unsaturated molecules while alkylation combines an unsaturated molecule with a saturated one.

The B.B. (butane-butene) mixture present in the reflux of cracked gasoline stabilization, is a suitable charging stock for nonselective alkylation. The substitution of isobutene for one of the hydrogen atoms on an isobutane molecule by alkylation yields an isooctane molecule. Subsequent hydrogenation is not necessary.[10]

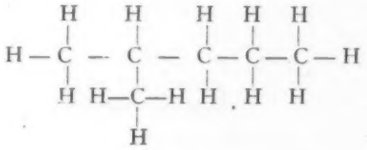
Represented below are some of the reactions which occur in alkylation processes:



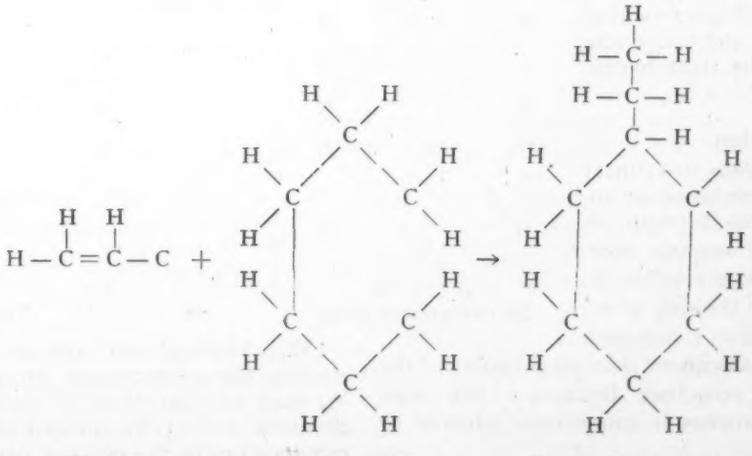
PROPENE ISOBUTANE 2,2,3-TRIMETHYL BUTANE (*Triptane*)



PROPENE PROPANE 2,3-DIMETHYL BUTANE



2-METHYL PENTANE



ETHENE CYCLOHEXANE ETHYL CYCLOHEXANE

Polymerization, alkylation and isomerization are processes which convert products of relatively low value into liquids having a high value. Prior to the development of these synthetic methods the gaseous hydrocarbons from refineries were used as fuel gases and in some instances wasted. Alkylation methods have very much enhanced the value of light hydrocarbon gases. Figure 12 is a simplified flow diagram of the Hydrogen Fluoride Alkylation Process.

Isomerization

Isomerization may be defined as the alteration of the molecular structure of an organic compound without changing the number of carbon and hydrogen atoms in the compound. Thus a process which changes normal butane into isobutane is an isomerization process. The improvement which results from the thermal cracking or reforming of low-octane straight-run gasoline and naphthas is no doubt to a considerable extent due to the isomerization of pentane, hexane heptane, octane, etc.

In catalytic isomerization many of the catalysts which have been used for alkylation reactions have also proven successful to some degree in isomerization. Mixed catalysts of copper sulfate, aluminum chloride, hydrochloric acid and aluminum chloride have been used with 67 to 74 percent conversion of normal butane to isobutane. Figure 13 is a flow diagram of a Butane Isomerization Process, The butane charge is passed through the saturator containing granular aluminum chloride. The stream from the saturator containing make-up aluminum chloride from the bottom of the aluminum chloride recovery tower enters the top of the reactor where it is mixed with anhydrous hydrogen chloride. From the reactor the stream passes to the recovery columns. The hydrocarbon is neutralized with caustic and then fractionated. The isobutane is removed and the normal butane is sent back through the system. Fifty percent conversion per pass of normal to isobutane is obtained at 125 to 150° F. temperature and up to 500 psi pressure. The catalyst is good for about 50 gallons of isobutane per pound of catalyst.

Since the isooctane processes employing polymerization and alkylation both require isobutane or isobutene as charge material, isomerization may be used to an advantage in conjunction with these processes. A higher yield of aviation blending stock and better economic utilization of the light hydrocarbon results.[11, 12, 13, 14]

Aromatization

The term *aromatization* in refinery practice refers to the formation of unsaturated ring structures belonging to the benzene family of organic compounds. The aromatization reaction involves the formation of the ring structure from straight-chain compounds and simultaneous or subsequent dehydrogenation to the aromatic unsaturated structure. Because of the steps in the reaction the process is sometimes referred to as *dehydrocyclization.*

Many of the aromatic compounds and their derivatives have high octane value, good blending value and good susceptibility to tetraethyl lead.

Until recent years the principal source of aromatic compounds was from the distillation of soft coal. During the war the chief source of toluene, an aromatic compound, was from the aromatization of petroleum hydrocarbons. Toluene is used in the manufacture of high explosives such as trinitrotoluene.

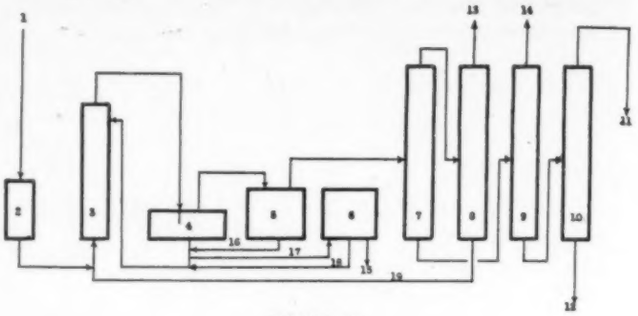
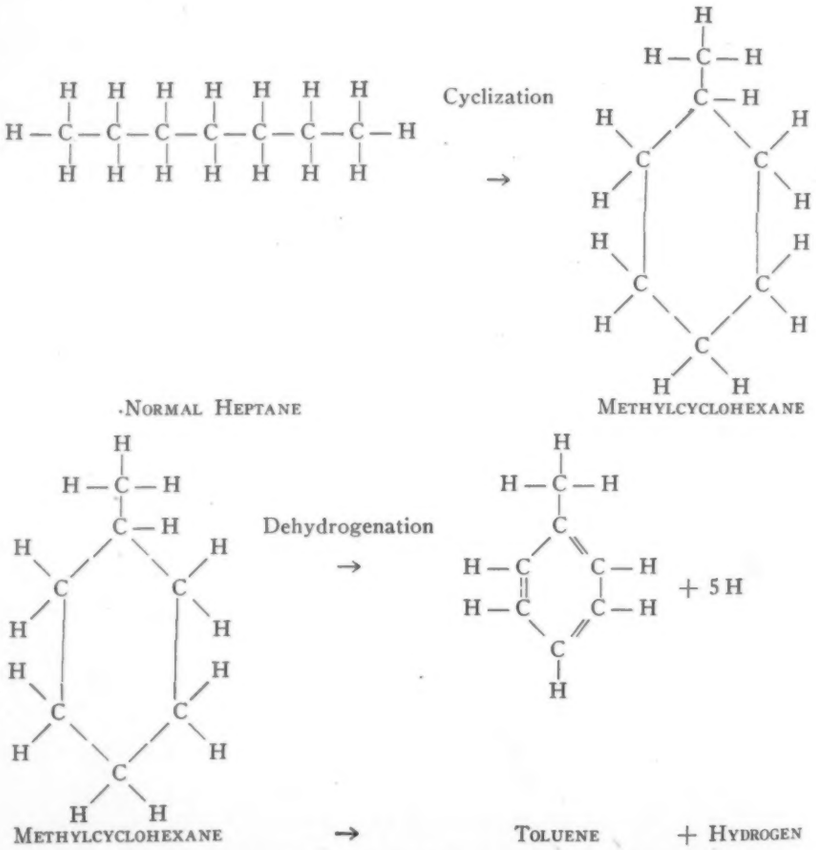


FIGURE 12
Hydrogen Fluoride Alkylation Process
1 Charge; 2 Charge Dryer; 3 Reactor; 4 Acid Settler; 5 Defluorinating System; 6 Acid Purification System; 7 Deisobutanizer; 8 Depropanizer; 9 Debutanizer; 10 Alkylate Fractionater; 11 Aviation Alkylate; 12 Heavy Alkylate; 13 Propane; 14 Normal Butane; 15 Waste; 16 Hydrogen Fluoride; 17 Spent Acid; 18 Purified Acid; 19 Recycle Isobutane.

In the Hydroforming process (see Figure 4, Chapter V) both the cyclization and the dehydrogenation of heptane is effected. Toluene results from the dehydrogenation of methylcyclohexane. The reactions are represented as follows:



Other thermal and catalytic cracking processes, including the cycloversion process (Figure 5, Chapter V) may be controlled to yield a high percentage of aromatic and cyclic compounds. The type of charge, temperature of the reactor, pressure, and time of con-

tact with the catalyst determines to what extent aromatization will be accomplished.

In toluene manufacture the aromatic distillate from the Hydroforming process, is called *hydroformate*. It is subjected to solvent refining methods and special distillation purification methods such as Shell Oil

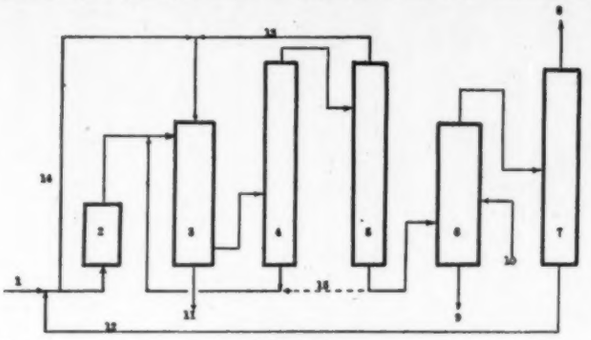
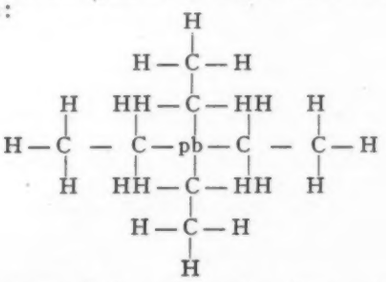


FIGURE 13
Butane Isomerization Process
1 Charge; 2 Aluminum Chloride Saturator; 3 Reactor; 4 Aluminum Chloride Recovery Column; 5 Hydrogen Chloride Recovery Column; 6 Caustic Scrubber; 7 Fractionator; 8 Isobutane; 9 Spent Caustic; 10 Virgin Caustic; 11 Sludge; 12 Normal Butane Recycle; 13 Hydrogen Chloride Recycle; 14 Hydrogen Chloride Make Up; 15 Hydrocarbon Complex Recycle.

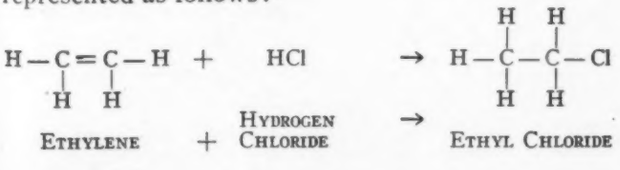
Company's extractive distilation[15] and azeotropic distillation.[16] Other branched-chain aromatics including benzene, xylenes, ethyl-benzene, propyl-benzene and isopropyl-benzene (cumene) are by-products which may be used as aviation blending materials.

Tetraethyl Lead and Other Additives

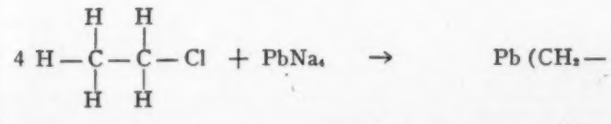
Before the technique of producing tailor-made molecules from petroleum had become fairly well known to refiners, trial-and-error experimentation had found that certain metallic-organic compounds, particularly those containing lead, when added in very small concentrations, were very successful in lessening the knocking tendency of gasoline. Of very many compounds tested for their anti-knock properties, tetraethyl lead is so far the best available, even when used in concentrations under 0.1 percent by volume. The compound is represented structurally as follows:



The compound is made by first chlorinating ethylene, and then causing the ethyl chloride to react with an alloy of lead and sodium. The reactions are represented as follows:



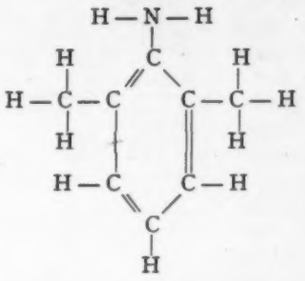
ETHYLENE + HYDROGEN CHLORIDE → ETHYL CHLORIDE



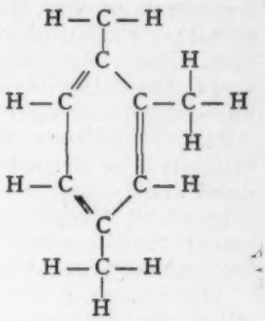
4 ETHYL CHLORIDES + LEAD-SODIUM ALLOY → TETRAETHYL LEAD + SALT (SODIUM CHLORIDE)

Tetraethyl lead is a colorless fluid having a sweet odor. As prepared for blending into motor and aviation gasoline, it contains ethylene bromide, made from refinery gas and bromine extracted from sea water, ethylene dichloride, kerosine, bromonaphthalene and a dye.

Several of the aromatic amines have been found to have powerful anti-knock properties. Xylidine, produced by the combination of xylenes and ammonia is known as CS (cumene substitute). Two of the xylidines are represented structurally as follows:



2, 6-XYLIDINE



2, 4-XYLIDINE

Aniline has also been found to be a high anti-knock compound, but is not used because it lacks sufficient solubility in paraffin hydrocarbons at low temperatures.

Triptane, 2,2,3-trimethyl butane, has been known for a number of years to possess the highest anti-detonating characteristics of any known hydrocarbon. The cost of production by known methods makes the cost for aviation fuels prohibitive, however, vigorous research which has been going on during and since the war, promises to make triptane available for super-fuels of the future.[17]

Injection of water into the air-fuel mixture of aircraft engines increases power and anti-knock properties. Alcohol and alcohol-water mixtures have also been used successfully as anti-knock additives.

Iron carbonyl compounds, of which three have been investigated, impart anti-knock properties when blended in hydrocarbon fuels. Iron, tetracarbonyl, pentacarbonyl and diferrononacarbonyl are the three iron compounds which have been investigated with regard to their possible use as anti-detonating agents in gasoline. The pentacarbonyl, a yellow viscous liquid with a boiling point of 217° F., is the most effective of the three compounds. Three cubic centimeters per gallon in a typical gasoline is said to increase the octane value from 58 to 96.[18,19] The iron carbonyl compounds are not likely to be of practical value as anti-knock additives, unless they can be made to resist decomposition when exposed to light and air. They are very unstable.

Ethers, ketones, and alcohols have also been used in aviation blends as high-octane blending agents. Since these compounds are in part oxidized, containing at least one atom of oxygen in the molecule, they are not preferred. The oxygen increases the weight per gallon. This is a very important factor in aircraft fuels. The oxygen also decreases the calorific value.

Table 8 lists some of the properties of the compounds mentioned in this chapter.

Gum Inhibitors

Many compounds have been tested with respect to their value in retarding oxidation of unstable molecules in gasoline and the resulting formation of troublesome gum. Aminophenol derivatives seem to be most effective, accomplishing the desired results when blended in gasoline in concentrations less than one pound per 5000 gallons of gasoline. These compounds prevent the oxidation of the gasoline only for a limited time. After the inhibitor becomes exhausted by becoming oxidized itself, gum formation proceeds at a rapid rate. Inhibitors usually are blended in the gasoline simultaneously with the tetraethyl lead.

TABLE 8

Aviation Gasoline Blending Agents

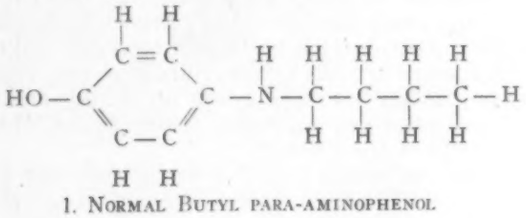
COMPOUND NAME	Boiling Point	Freezing Point	Reid Vapor Pressure	Calorific Value	Weight Per U.S. Gal.	Specific Gravity	Octane Value
Benzene	176*	42	3.4	17,200	7.34	0.879	100+R
Cyclohexane	177	44	3.5	18,800	6.50	0.767	110 R
Methyl Alcohol	148	—144	4.5	8,400	6.62	0.793	98 M
Ethyl Alcohol	173	—176	2.5	11,600	6.58	0.789	99 M
Isooctane or 2, 2, 4 Trimethyl Pentane	211	—161	1.8	19,100	5.77	0.692	100 M
Isooctane or 2, 2, 3 Trimethyl Pentane	230	—170	1.2	19,100	5.98	0.716	100 M
Isooctane or 2, 3, 3 Trimethyl Pentant	239	—151	0.9	19,100	6.06	0.726	100 M
Noehexane or 2, 2 Dimethyl Butane	122	—148	10.0	19,200	5.42	0.649	97 M
Xylene (ortho)	292	— 13	0.3	17,600	7.34	0.880	100+R
Xylene (meta)	282	— 54	0.35	17,600	7.21	0.864	100+R
Xylene (para)	281	+ 56	0.35	17,600	7.19	0.861	100+R
Cumene Substitute or 2, 4, Xylidine	420	....	0.005	15,700	8.13	0.974	....
Cumene Substitute or 2, 6, Xylidine	422	....	0.005	15,700	8.17	0.979	....
Cumene or Isopropyl Benzene	306	—141	0.2	17,700	7.19	0.862	99 M
Triptant or 2, 2, 3-Trimethyl Butane	178	— 13	3.6	19,100	5.76	0.690	140 M
Isopentant or 2, Methyl Butane	82	—235	22.0	19,300	5.17	0.620	104 M
Neopentant or 2, 2-Dimethyl Propane	50	....	37.0	.....	....	0.613	83 M
Tetra-ethyl-lead	360**	—213	0.02	.....	13.80	1.653	....
Ethyl Cyclohexane	269	....	....	.....	....	0.7878	41 M
Methyl Cyclohexane	214	....	1.2	.....	....	0.7692	71 M
Toluene	231	—139	1.2	17,400	7.23	0.867	100 R
Aniline	364	21	0.04	15,000	8.53	1.022	....

* Temperatures—°F. R—Research Method. M—Motor Method.

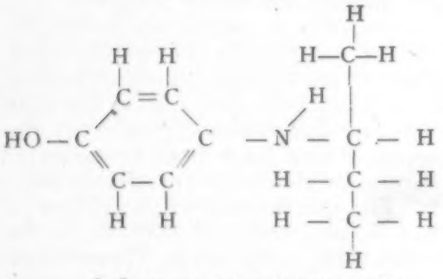
The following is a list of some of the inhibitors which are being used in both aviation fuels and automotive fuels.

1. Normal butyl para-aminophenol
2. Isobutyl para-aminophenol
3. Ortho cresol (also meta and para)
4. Monobenzyl para-aminophenol
5. Di-secondary butyl para phenylene diamine
6. Do-methyl tertiary butyl phenol

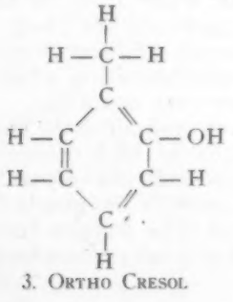
The structural formulas for the first three in the above list are as follows:



1. Normal Butyl para-aminophenol



2. Isobutyl para aminophenol



3. Ortho Cresol

Safety Aviation Fuels

Aviation engineers desire for the future the best that can be made available in aviation fuels, including all of the wartime developments, at prices comparable to prewar fuels. They prefer no tetraethyl lead, at least less than is now being used. They maintain that the decomposition products of tetraethyl lead increases engine-maintenance costs.

Research is in progress to make available safety fuels for use in injection-fuel-type engines. Only relatively high boiling hydrocarbons are included. The high flash point of such fuels, although high in octane value, make them comparable to kerosine as regards safety in handling. With such fuels the fire hazard in air travel is much reduced.[20,21]

The jet-propulsion engine is also demanding much attention from aircraft and fuel-research organizations. At present, however, the application of jet propulsion is principally for military aircraft.

At least for the immediate future, and perhaps for the next five years at least, commercial aviation gasoline will be made by refineries according to the methods touched upon in this chapter.

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Water Treatment In Refineries

R. W. KELLY*, Dearborn Chemical Company

* Delivered before Regional Technical Meeting of the Western Petroleum Refiners Association, Lansing, Michigan, June 20, 1946.

THE subject of water treatment, of course, covers many phases and has been the object of much study by many competent people. As time goes on, many new processes and industries require its use for processing, cooling and transmission of heat. This makes the subject so large that I shall attempt to cover only that phase which pertains to the oil refining industry.

Feed water for boilers is treated by external softeners and by internaal treatment. The lime-soda ash softener makes use of a reactor of sufficient size to allow adequate reaction time between the water and the chemicals used. Lime is used to reduce the bicarbonates to carbonates, which in turn are insoluble and will drop out as a sludge. Soda ash is used to convert the non-carbonate or permanent hardness to the more soluble sodium salts. The resultant insoluble carbonates will drop out as a sludge with the other carbonates occurring originally in the water. Generally a coagulant such as sodium aluminate or alum is used to increase particle size in the softener and thus improve its efficiency. The treated water is finally passed through a filter to remove last traces of suspended matter. The lime-soda ash softener has the advantage over the zeolite softener in that it actually reduces the soluble solids content.

A zeolite softener merely exchanges the calcium and magnesium present in the water for the more soluble sodium in the zeolite. After all of the sodium in the zeolite is used, the softener is taken off the line and regenerated. Regeneration is brought about by using salt to replace the calcium and magnesium in the zeolite with sodium. The softener is then washed free of all the calcium and magnesium and then put back in service and the cycle repeated. A zeolite softener has an advantage over the lime-soda ash softener in that it requires very little control. It has the disadvantage of bringing about a much higher alkalinity in systems where high carbonate water is used.

Internal treatment is generally necessary in boilers whether or not an external softener is used. Lime-soda ash softened water always contains some encrusting solids which necessitate treatment. Zeolite-softened water often contains some hardness and usually contains so much soda alkalinity that treatment for prevention of caustic embrittlement is necessary.

Materials commonly used internally for scale control are sodium phosphates, soda ash, and organics such as tannin and starch, which due to their surface active properties, keep the tri-calcium phosphate and calcium carbonate sludge in such a fluid condition that it will be non-adherent to the metal and can be easily removed by blow-down.

Another problem to be overcome by internal treatment is pitting, which is caused by oxygen or an acid condition in the boiler, or a combination of both. Sodium sulphite and tannin generally are used for absorption of oxygen and sufficent soda ash should be used to neutralize any acid condition.

Caustic Embrittlement

Caustic embrittlement is an old bugaboo that has been hanging over the heads of boiler operators for many years. It is generally accepted that this condition can only exist where there is a high causticity plus some soluble silica and, generally, leaks around rivets or in seams. If these conditions exist in a boiler, it can now definitely be determined whether the water is embrittling or not by the use of the embrittlement detector developed by the Bureau of Mines. Sulphates have been set up by the ASME code as a standard for prevention of caustic embrittlement. Phosphates and tannins have been shown to have merit. More recently, soluble nitrates have been proven to be the most generally satisfactory for prevention of embrittlement.

Each one of the schemes or materials mentioned for boiler-water treatment, has a definite purpose. No one of these alone is an all-inclusive cure-all, but each has its use. I should like to emphasize that along with the proper treatment scheme and proper treating materials that this all would be wasted unless there is adequate control.

As an illustration of how investigation plus control may pay off, I have in mind a small gasoline plant recently built in Oklahoma. Two water wells were drilled fairly close together and normally it would be assumed they would produce the same water. On making a mineral analysis, it was found that there was sufficient alkali in one to counteract the effect of the scale-forming material in the other. Water from these wells was blended and used in the cooling system and picked up there and then used for feed water in the boilers. By use of a small amount of organic and glass-type phosphate in the cooling pond, it was possible to control scale formation both in the cooling system and the boilers. This, of course, was only possible by sufficient testing so that adequate control should be maintained.

Along with water treatment and control, there is the question of blow down. At the present time in the Mid-Continent area which I cover, I believe that there are 75 percent of all boilers, including small 65-horsepower oil-field-type boilers, equipped with continuous surface blow downs. I have heard estimates that continuous surface blow down will cut down the amount of water wasted as much as 50 percent and still maintain good conditions in the boiler. Once these blow downs are installed, and this many times over the operator's dead body, they will never be removed as he will find out that they help his work greatly and the management will find they are getting cheaper steam and improved operation.

Cooling Water

Treatment of cooling water internally is done with the exact opposite purpose in mind of that in a boiler. In a

boiler, water is treated to precipitate out all incrusting solids and condition them so that they may be blown down from the boiler. In a cooling-water system, the aim is to keep all solids in solution or in suspension.

Accurate predictions of scale formation by a particular water in a system may be made by use of Langolier's Equation, provided alkalinity, calcium content, total dissolved solids, pH and temperature are known. This equation is entirely reliable where the above conditions can be determined. In ordinary plant operation, the problem is not quite as simple as conditions vary so much even in one system. In refinery operation there may be skin temperatures on cooling tubes as high as 400 or 500 degrees, and even higher; while in the same system, water temperatures may be as low as 60 or 70 degrees. In this case the water at the low temperatures probably would be corrosive and pick up scale-forming material which it would then deposit at the point of high temperature. In gasoline plants especially, the most aggravating thing to contend with is coverage. In these plants temperature differences are not as great and maximum temperatures are not as high as in refineries; however, most of the cooling is done by a water spray falling down over an open-bundle exchanger. Here, even though the top of the tubes may be completely covered, the bottom will not be, and consequently the top side of the tubes will be clean and the bottom may be covered by scale. This bottom scale usually is not of sufficient magnitude to cause great difficulty. Scale formation in any cooling system may be eliminated, but usually the deciding factor on treatment is cost of treatment versus the efficiency needed. Ordinarily, a small amount of scale is beneficial in that it will protect the equipment from corrosion and will not materially cut down the efficiency of the cooling equipment.

I think the following results, which were obtained in two separate plants, will illustrate my point:

Cromwell Cooling System

	P	M	H	Cl	Special Phosphate p.p.m.	Cl Conc.	H Conc.
Make Up.....	....	12.5	10.5	6.0	.....	.....	.....
Coil Pit.....	2.6	28.4	20.0	19.0	3	3.2	2.0

Readings are in grains per gallon unless otherwise specified.

Skiatook Cooling System

	P	M	H	Cl	Special Phosphate p.p.m.	Cl Conc.	H Conc.
Make Up.....	.....	35	43	15	4	.....	.....
System.....	3	118	236	76	4	5.1	5.5

Readings are in parts per million.

The first set of results were obtained in a gasoline plant in which liquid petroleum gases were being made and efficient cooling was a necessity. Based on the chloride concentration of 3.2 the hardness in the coil pit should be 3.2 times 10, or 32. for 100 percent treatment efficiency. As it was, about 25 percent of the incrusting solids were being dropped out of solution and possibly adhering to the hot cooling surfaces. This loss of solids, however, was not enough to materially decrease efficiency.

The second set of results were obtained in a refinery and show that more incrusting solids were being held up than theoretically were in the system. In this system there were some shell-and-tube exchangers overloaded and operated with such low water rates that they became badly scaled in a few weeks and necessitated a shut down. What I have tried to show is, that in a cooling system, accurate predictions based on a water analysis, can be made but it is also necessary to know operating conditions in the plant.

After a water analysis has been made and a survey of operating conditions compiled, a treatment process has to be decided on that will provide satisfactory operating conditions in the plant and still be of such a nature that it can be controlled and operated efficiently by the personnel on hand.

There are places where an external softener using lime alone is employed. Here very accurate and almost constant control is necessary, as an overdose of lime might bring about an after precipitation that could be worse than would occur from the original water. Very seldom is lime-soda ash softening warranted for cooling water. It is seldom that extremely high sulfate water occurs, and where it does a zeolite softener would probably be more feasible due to its ease of operation.

Zeolite softening is occasionally used for softening cooling water but there is always the possibility of dezincification of brass fittings. In all cases where there is a cooling tower, the high alkalinity of the water will cause delignification of the wood, which will eventually result in a fuzzy board and finally a pile of fuzz, as all of the binder holding the fibers together will have disappeared.

It is my opinion that internal treatment is the process most commonly used on cooling systems. The glass-type phosphates and certain surface-active organics are used either separately, or in conjunction. These in turn are supplemented in many cases by sulphuric acid. Generally, the only natural elements in water which give scale trouble are the carbonates of calcium and magnesium, which after being converged to the sulphates give much less trouble. Sulphuric acid alone, or in conjunction with a supplementary treatment, must be controlled very closely or the equipment may be eaten up by too much acid, or the sulphates may reach a stage where they will drop out and, of course, form a scale which can only be removed by hammer and chisel. A standard usually set up for sulphate concentration in a system is 1500 parts per million. The control for acid is a carbonate figure of 30 to 50 parts per million.

The use of glass-type phosphates is limited by the amount of material they will hold up under the temperatures encountered in a refinery and also the amount of reversion occurring in a circulating system.

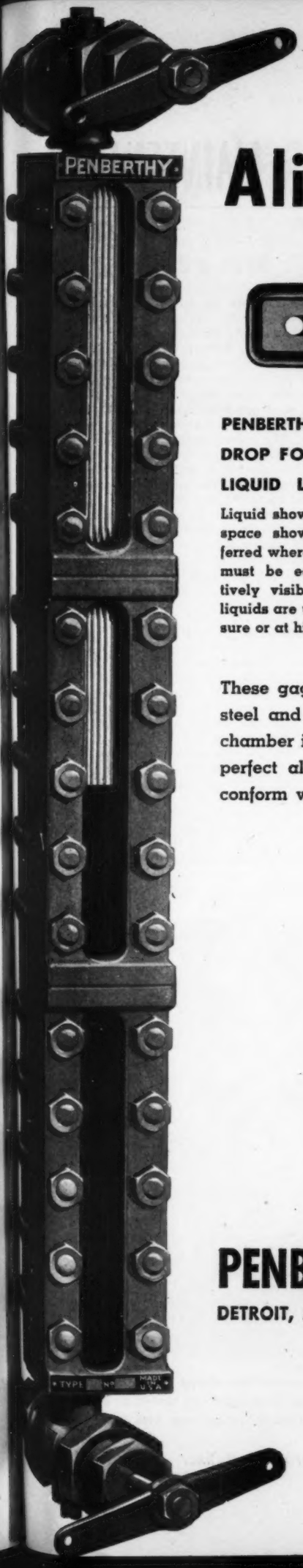
Time and temperature are the main controlling factors on this conversion rate. Of course, after reversion from the glass type to the ortho, the phosphate acts as a softening agent and ceases to be of any value as a cooling-water treatment. This softening action may be neglected unless the reversion is very rapid as the amount of phosphate used is very small. Phosphate dosage is usually about 1 or 2 parts per million based on the raw water, or sufficient to maintain a 3 to 5 parts per million in the system. In a compounded treatment this amounts to only about 0.1 pounds per 1,000 gallons of make-up water.

The success of any of these cooling-water-treating processes is dependent on control. Theoretically, if there was no windage loss, leaks or purge from a tower, you would eventually wind up with solid mineral and no water. Of course this never occurs as there are always leaks and windage losses but there is seldom any controlled purge. Most of the water lost from a tower is due to evaporation with all of the minerals being left behind. Seldom does an operator think of operating a boiler with no blow-down, and, at the same time, seldom does he think of purging his cooling-water system. Treatment control and concentration control are both necessary.

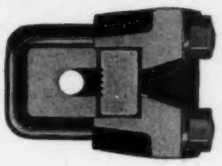
Algae, or moss, many times gives considerable difficulty by fouling equipment so that both air and water circulation may be impaired and heat transfer be limited. Chlorine and chlorine liberating compounds have been used for many years. Chlorine is extremely effective but it does have the disadvantage that it will disappear into the air quite rapidly on aeration of the water. Copper sulphate, potassium permanganate and certain mercury compounds have been used In recent years sodium pentachlor phenate has been used very successfully. There is a tendency where an algecide is used continuously for the algae to build up an immunity. Most plants I know of are slug treated and doing a satisfactory job that is much more economical than continuous treatment.

Feeding Equipment

There are many problems which I have not touched and probably some which I have stressed too much. I have made many statements as statements of fact without backing them up by reasons. This is very bad from a technical or practical viewpoint, but I felt it necessary in order to try to present a complete picture. There is one thought which I would like to leave with you: that is, that any approach to a water-treating problem will only be as successful as the degree of control kept on it.



Alike in Quality



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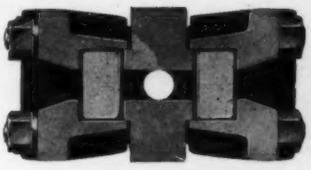

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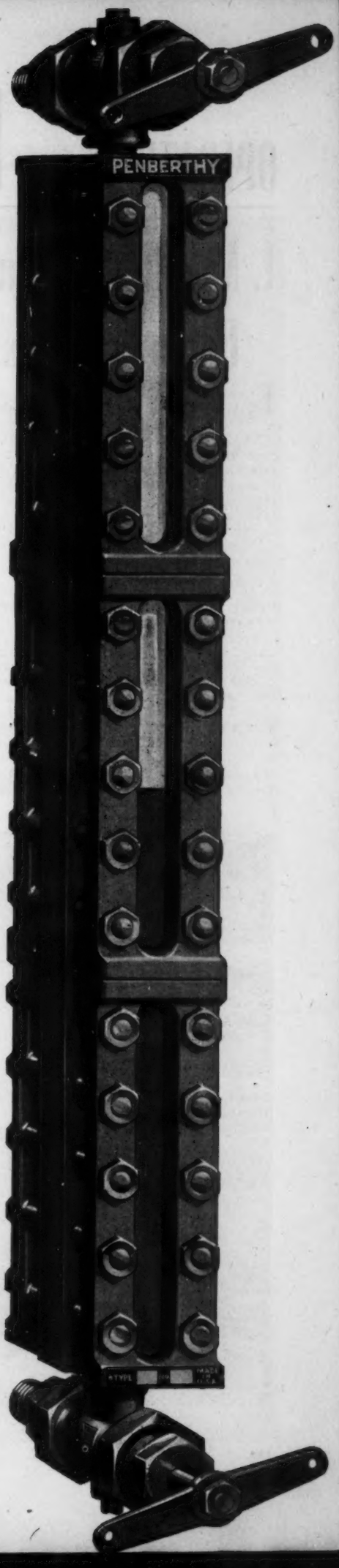

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PENBERTHY PRODUCTS

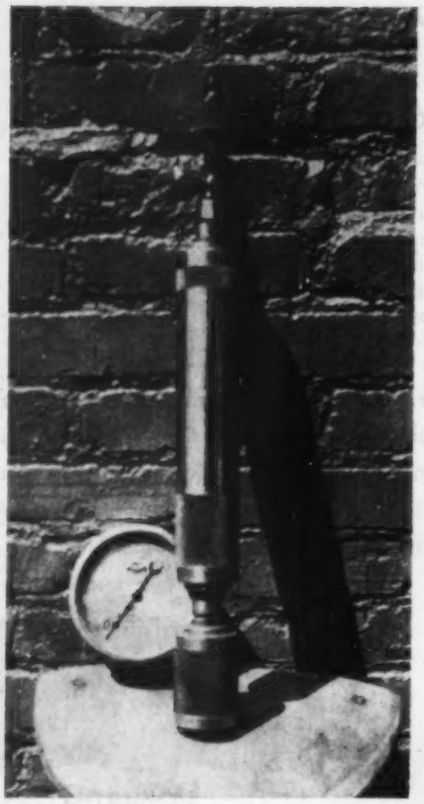
OPERATION HOW TO DO IT MAINTENANCE

1. Needle Valve on Vapor Pressure Bomb Prevents Gauge Damage

IN MAKING a vapor pressure test by the Reid Method as required by the ASTM Designation D 323-41, the vapor-pressure bomb must be turned upside down and shaken vigorously several times. The pressure gauge required for this test must be of the Bourdon spring type and some 4½ to 5½ inches in diameter.

This severe shaking of the assembled bomb causes wide fluctuations of the hair spring and hand on the gauge and as the gauge is a delicate instrument, it usually suffers some damage or deviation from accuracy.

In order to eliminate this abuse of the gauge and its working parts, a ¼-inch needle valve may be attached to the air chamber of the bomb in the top bushing and a standard ¼-inch coupling placed on it. The vapor pressure bomb may then be made up with its sample and immersed in the bath and shaken as frequently as desired. The gauge need not be attached until a reading is desired. If a check is desired, the gauge may be removed or shaken with the bomb for the final and last check.



Views of vapor-pressure bomb with and without gauge attached.

This method of fitting the gauge is permitted by provisions in Paragraph 2 (A) of the test and reduces the wear and tear on the gauge as well as permits greater accuracy in the test.

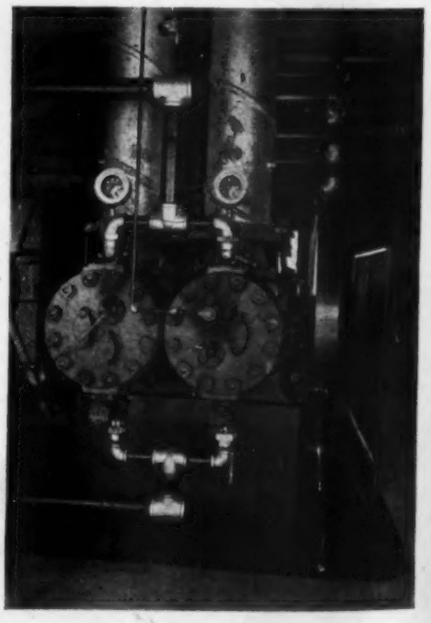
2. Exhaust Provides Cooling System

HEAT from the exhaust pipes is utilized to set up a ventilating current which draws air around the engine cylinders and thence through ducts to the outside of the station building. Engine exhausts are carried vertically from the ports to a point above the station roof, and there tied to muffler manifolds which serve the dual purpose of quieting the surge and preventing the entry of rain into the pipe.

Each exhaust pipe is enclosed in a short portion of light pipe four inches larger than the outside diameter of the exhaust. These covers are carried on spiders at the exhaust flange, and are provided with conical shields which tend to prevent the entry of air from above, forcing the draft to enter from around the engine.

The air in the annulus between exhaust pipe and shield draws in at the base fresh air from the station. The rate of flow is dependent upon the difference in temperature between the air in the annulus and the atmosphere, with only relatively slight heat being radiated to the outer or shielding pipe.

The shield is carried through the roof, terminating three inches short of a



Pipes around the exhaust pipes provide an annulus in which ascending heated air is replaced by air from the engine room, with cooling effect.

Win a Bond

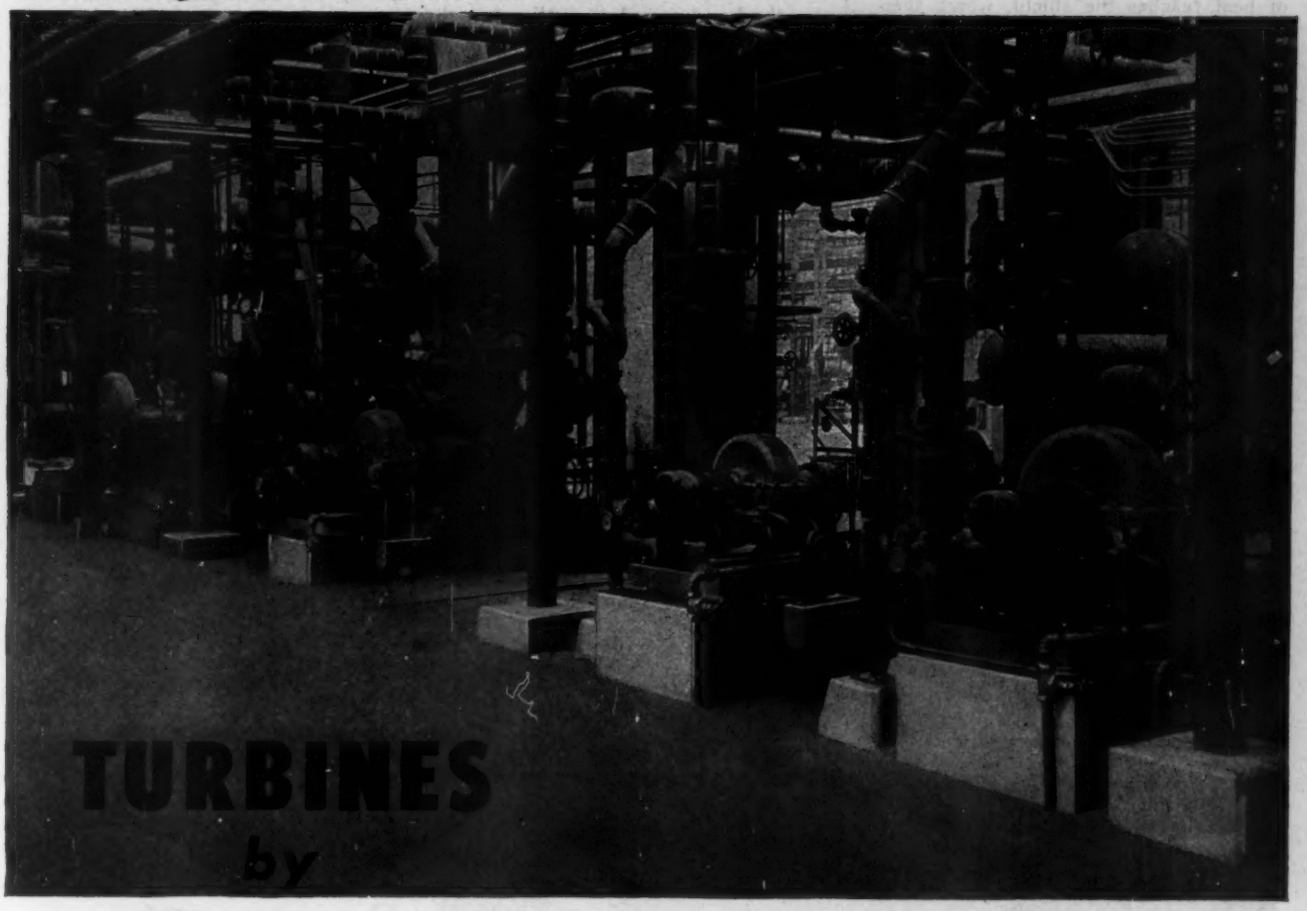
EACH month the operating personnel in the refining, cycling and natural-gasoline plants determine the winner of a War Bond, maturity value $25.00.

Superintendents, assistant superintendents and foremen (subscribers as well as non-subscribers) become a jury to select the most practical contribution to this department on maintenance and operation. The editors rotate voting among men qualified to determine the rating.

This award is in addition to payment for the article. The methods of solving plant operation and maintenance problems come from the personnel of the industry. Items provided by Petroleum Refiner staff members will not be eligible.

Send contributions to Petroleum Refiner, P. O. Box 2608, Houston 1, Texas.

Ganging up FOR MORE GALLONS PER HOUR



Elliott

Here's a line-up that assures a high score in output volume. Elliott turbines — hundreds of them — drive the main process pumps and other important equipment at a western "cat-cracker" plant. It's one more of the many cases where an important refinery standardizes on tough, trouble-free Elliott turbines for responsible tasks.

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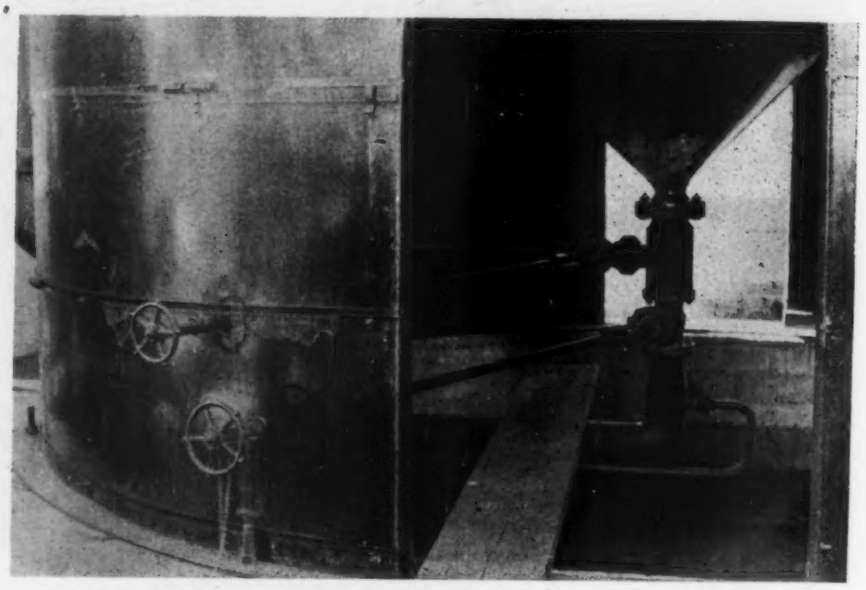
conical shield, welded snugly to the higher riser of the exhaust line. The heated air is discharged under this shield, which serves to prevent entry of rain down the annulus.

By closing the area of this annulus during winter months, a greater amount of heat reaches the shield, which then becomes an effective hot-air radiator for warming the air within the station.

READERS ARE URGED TO CONTRIBUTE items to this department. Drawings or photographs are desired where practical. Payment for items accepted will be on a basis that will compensate for the time involved and in addition each contribution will be eligible to receive the bond award as outlined in the announcement on Page 146. Jury awards will be announced in the second issue after publication.

3. Remote Gate Control On Acid Sludge Tank

WHEN controlling any commodity by opening gates on piping attached to the cone base of separating or storage tanks where acids are present, remote hand valves afford comforting protection for workers. The commodity handled in the vessel illustrated is acid sludge being prepared for burning in heaters and pipe stills. The skirt of the vessel contains two openings sufficiently large for men to enter without difficulty to open valves when the stems are of the conventional type. To avoid accidents, the wheels are removed from the bronze valves and attached to extension stems which pass through the skirt of the tank, using holes drilled at a point most convenient for opening and closing. Extension stems at the point of attachment to the original valve stems have boxes broached to fit the stem of the valve and clamped with set screws to prevent them from becoming loosened while using.



Remote hand valves on acid tank.

Device for speedy cutting of gaskets 4 to 48 inches in diameter.

4. Gasket Cutter Speeds Plant Maintenance

REQUIRING large numbers of gaskets of various sizes for heat exchangers and similar equipment, the maintenance department of an Arkansas gasoline plant found that a simple type of gasket cutter provided wide flexibility and speeded up gasket cutting.

As shown in the accompanying photograph, with its designer-builder, Fred L. Strange, machinist of Stamps, Arkansas, the table of the cutter is made from a piece of ¾-inch plywood 5 feet square mounted on sturdy supports. Three of the corners of the table are rounded. One corner is left to support the base of the centering and material holding arm. The arm of 2-inch pipe is welded to an elbow and a flange, and the flange bolted to the remaining corner of the table. The centering and material-holding head is a tee welded on the arm with a threaded bolt through it having an offset fitting on the lower end for the cutting-head arm and the material-holding point. A set screw in the offset fitting permits adjustment of the length of the cutting head arm for the desired gasket diameter. The handwheel on the upper end of the bolt is used to set the centering point on the material. The cutter head on the end of the arm is made from an aluminum block fastened to the arm with a screw, and will hold a heavy type blade or a

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Heavy Wall Welding Necks

Type RO Manway Neck

Reinforcing Nozzle

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PROCESS INDUSTRIES

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- Condensers
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- Digesters
- Agitators
- Mixers
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- Softeners
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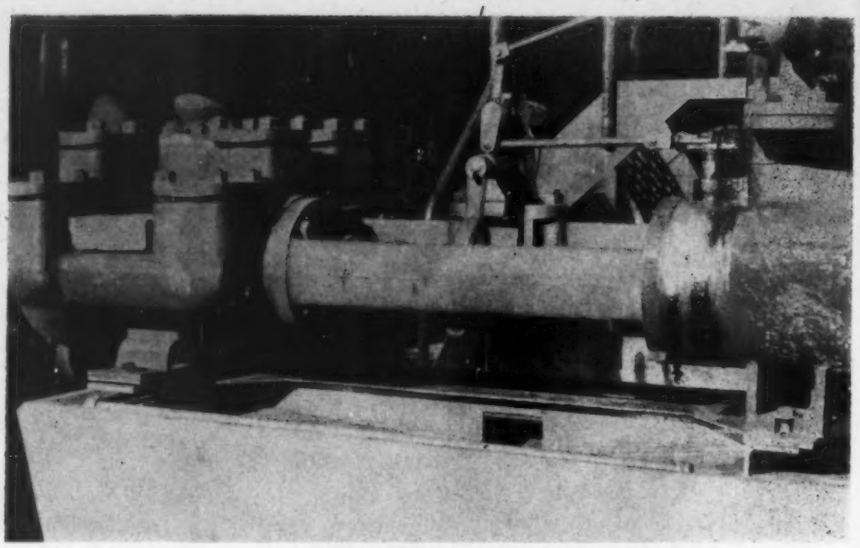
thin type, such as a razor blade, depending on the thickness of the gasket material. As the blade is fastened inside the block with screws and protrudes from the bottom the desired distance for cutting the material, the operator's hand is protetced from possible injury by the blade.

The gasket cutter will handle gaskets from 4 to 48 inches in diameter. If the gaskets requires strips or centers (bars). a steel straight-edge is used in conjunction with the cutter head, which can be removed from the arm. When a gasket is being cut from a roll of material, the operator must move the cutter around the table to cut the gasket; however, if the material is near the size of the gasket, the operator stands in one position and shifts the material held to the table by the centering head until the gasket is cut. Average length of time required to cut a heat exchanger gasket is about 7 minutes.



Pump foundation with plate steel instead of bolts.

5. Portable Battery For Starting Engines

INDIVIDUAL multicylinder engines may deliver more horsepower if a generator is not included. Obviously, this eliminates the battery ignition set, which is replaced with a high-tension magneto. Battery maintenance is reduced over the plant when several such engines are used to drive blowers, pumps and other machinery, and not equipped with generators and individual storage batteries. Del Valle Gasoline Company uses a number of individual gas engines for various purposes, all of which are equipped with magneto ignition, but have starting motors attached. To start these engines, heavy duty 12-volt batteries are maintained to full charge by the plant electrician, and in condition for instant use, when and if an engine is shut down for any reason. The engines have receptacle installed in the hood above the starting motor, with conventional heavy-duty cables to the motor and to a positive ground connection. The batteries are mounted on a wheelbarrow, fitted with a tray to receive the battery and which may be easily moved to any part of the plant with little effort. Extension cables are attached to the positive and negative posts of the battery with a plug-in attachment which carries both cables. For starting at will, a solenoid switch is attached in one of the cables which may be operated by pressing on the button on the switch, or operating a conventional button located on the engine at a convenient place.

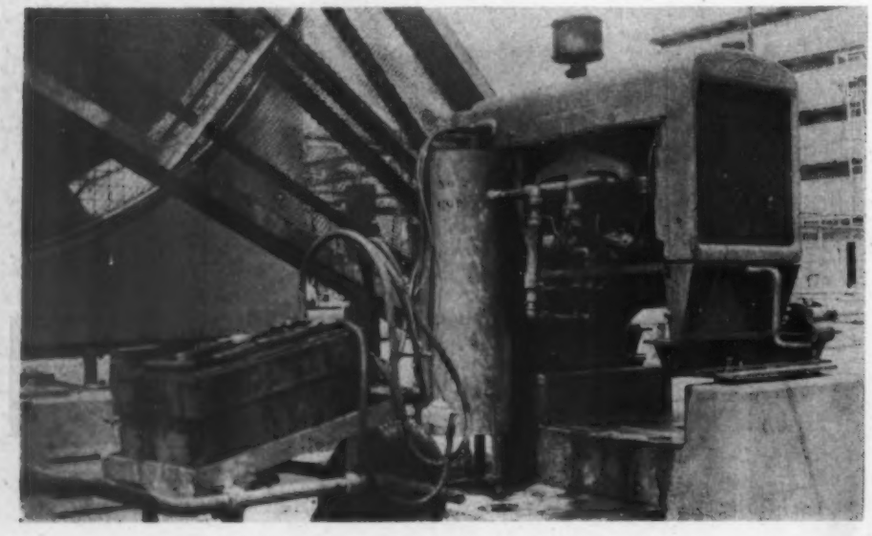
6. Pump Foundation For Light Units

ELIMINATION of imbedded foundation bolts in light-weight pump foundations has been obtained by a different type of mounting such equipment. The concrete block is poured of the conventional mix, with a structural steel sub-base included in the block as an integral part. The sub-base is made by joining two sections of I beams—laid closely together—with gusset plates which connect to channel-iron end pieces placed at right angles to the I beams. The sub-base as tailored for the individual pump so as to obtain the required dimensions and to supply contact support for the feet of the pump, both at the steam and the fluid ends.

In shaping the face of the block, in which the structural steel support is imbedded, it slopes from all directions toward the center in which the drain pipe is placed when the block is poured. Natural slope afforded by the design of the surface of the block provides means for the liquids to flow directly to the waste line, but if hold-up occurs, washing with flushing water is afforded with streams of water flowing through perforated pipe laid at the outer rim of the block. This water may, or may not be flowing constantly, depending upon the condition at the individual setting. If acid or alkaline solutions are handled by the pump, flushing has its advantages by eliminating puddles or surface film on the concrete.

7. Improved Shape For Pump Foundation

OBSERVING how tiring and difficult servicing of pumps can be when mechanics stand close to foundations which have vertical sides, the design engineers in a California plant decided upon a radical change in the shape of



Battery is moved to the engine for starting as required.

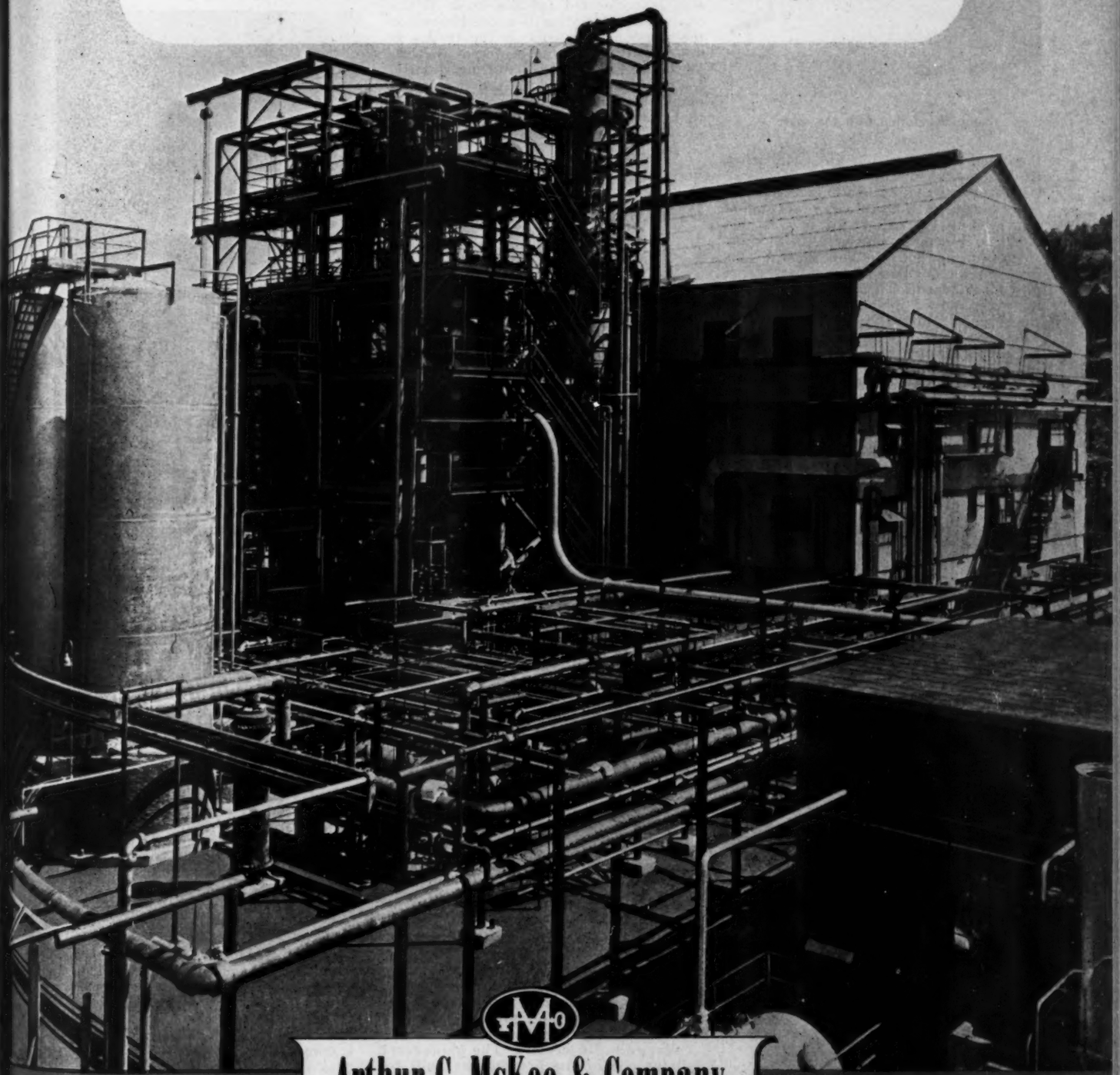
THE WINNER

A number of readers selected at random and asked to evaluate items printed in this department in May have indicated the award should go to Item No. 1—"High Pressure Steam Valve Gasket Repaired in Service." The bond award has been given to the contributor. This item was contributed by a member of our regular staff.

UNDIVIDED RESPONSIBILITY IN ONE ORGANIZATION

M·E·K SOLVENT DEWAXING PLANT

This 2000-barrel M. E. K. Solvent Dewaxing Plant (process licensed by Texaco Development Corporation) was recently completed by Arthur G. McKee & Company for The Pennzoil Company at Oil City, Pa. Design, engineering and construction were handled entirely within our own organization.



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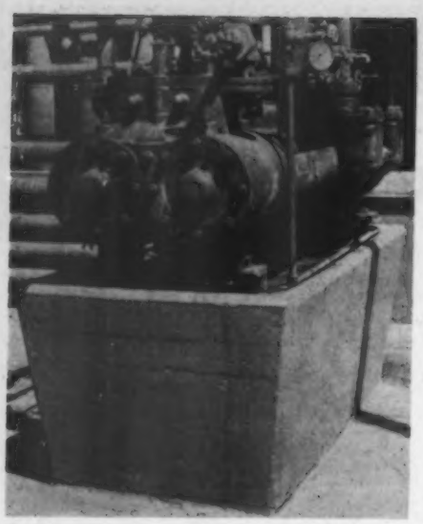


Pump foundation with toe room.

the concrete pump blocks. Comparing the ease by which one may stand against laboratory equipment with recessed toe spaces against the difficulty of standing against vertical walls, it was decided to pour the blocks with sloping sides. Forms built in the form of an inverted rectangular pyramid were employed in recent construction and gave approximately 3 inches more toe room than with straight sided foundations. Less back bending is necessary when packing stuffing boxes, tightening packing glands and doing general maintenance work, and a considerable saving of material is obtained with this type of foundation.

8. Improvised Trolley For Occasional Use

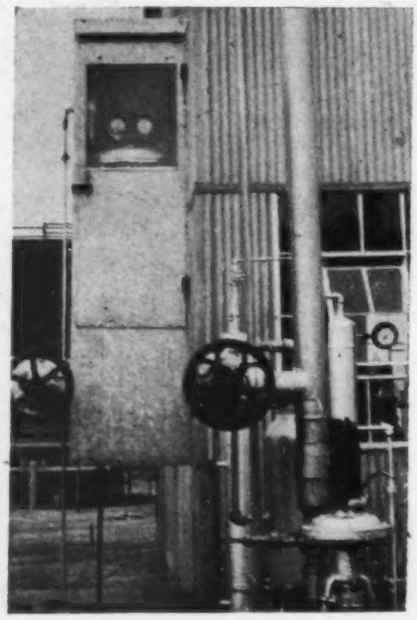
FOR lifting heavy equipment, such as pumps, turbines and the like during a refinery overhaul, it is not practical to erect permanent structures above the installations to use trolleys, as would be indicated in engine rooms, for example.

The roller is a piece of pipe.

Trolleys can be made up for use on heavy wood beams, which are erected and torn down before and after the overhaul. The trolley is made in this instance of a short nipple of 8-inch pipe. The length will be governed by the width of the beams to be used, but when using 8 by 10 beams, the 8-inch long nipple is used. End plates are made by cutting circular sheets of substantial steel, perforated with six holes, which are for a purpose as will be shown. The hub is made by passing a tube through both ends, in the exact middle, through which the axle is placed. Straps of steel attached to each end of the axle are joined at the lower end with a bar of steel to which a link, or ring is connected for the hook of the chain hoist. Hoisting is accomplished in the usual manner, but, if the trolley is not exactly above the center of the lift, or should the load need shifting slightly, a crow bar inserted in the perforated end holes provides a leverage point so that the mechanic may change the angle of lift, or center the trolley exactly where it is desired.

9. Steam Coils Prevent Regulator Freezing

A SHEET steel house completely enclosing a regulator setting solved the freezing problem for one operator. A few loops of copper tubing on the back of the house, which is the north side,

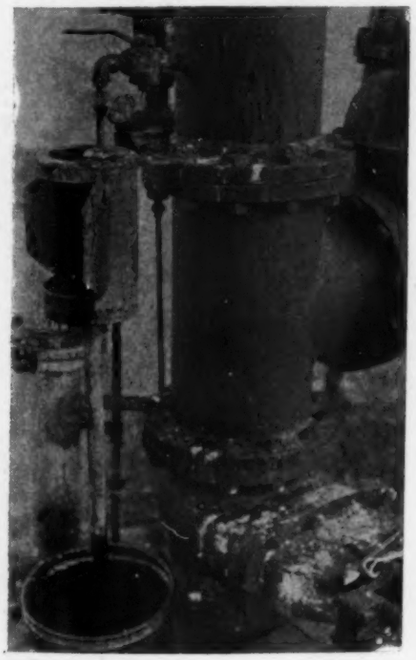


Steam-heated regulator house.

maintains the regulator and control equipment well above the freezing point even in zero weather. On some installations where the fluid in the main line is above the freezing point, the house retains the heat and prevents the controls from freezing up, and the heating coils are not necessary. The photograph shows one of the first houses built for this purpose. Since this one was built, a meter house manufacturer has taken over and is making them in quantity.

10. Device Confines Oil Spatter at Sample Cock

IN ORDER to hold to a minimum the splatter of oil that usually accompanies the drawing off of a sample from a high-pressure line containing a heavy oil, one company installed at each of the several sample cocks in the plant a small receptacle into which the sample container may be placed while the fluid is being withdrawn. The device consists of a short length of 4-inch pipe having a doorway cut out of its side and a

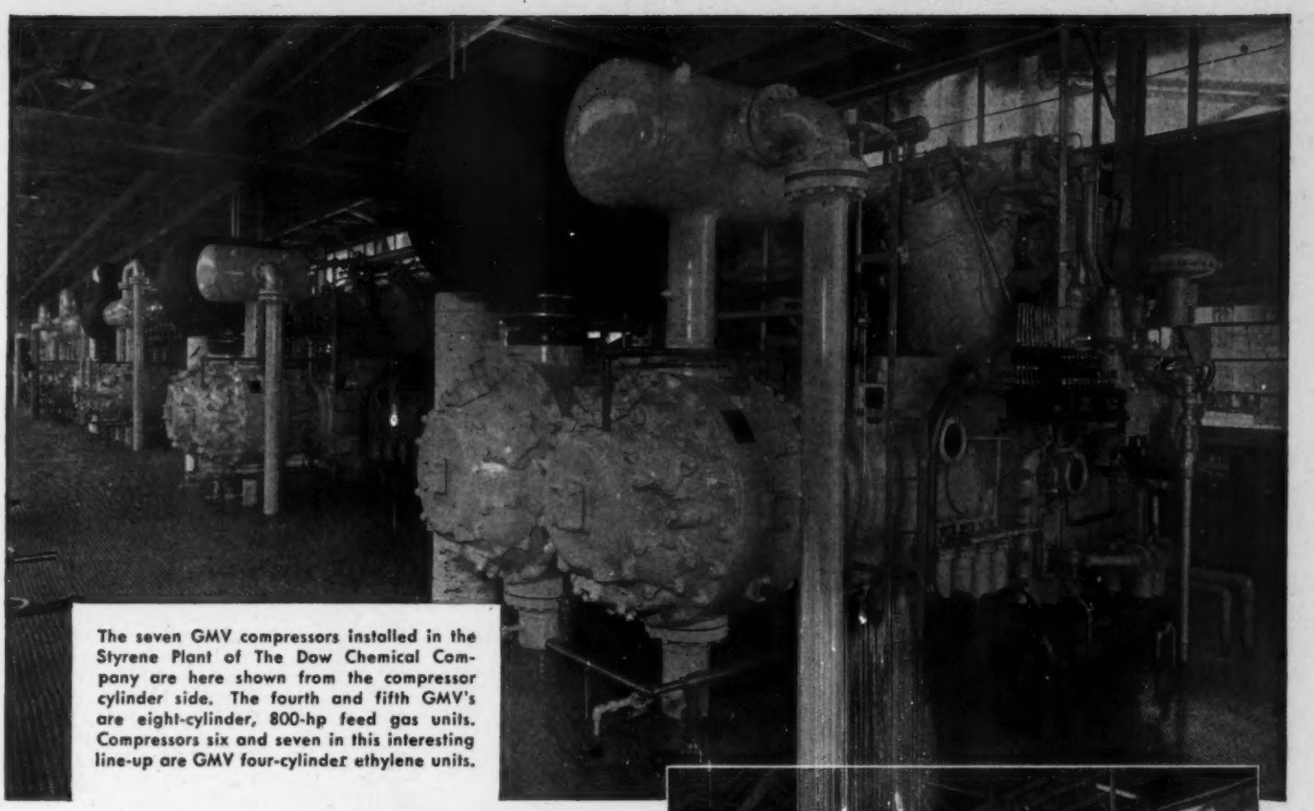


Prevents sample spatter.

funnel and tail pipe welded in at the bottom as shown in the illustration. The unit is hung on the sample cock line at any convenient height and beneath the tail pipe is placed a bucket or container which can be dumped periodically.

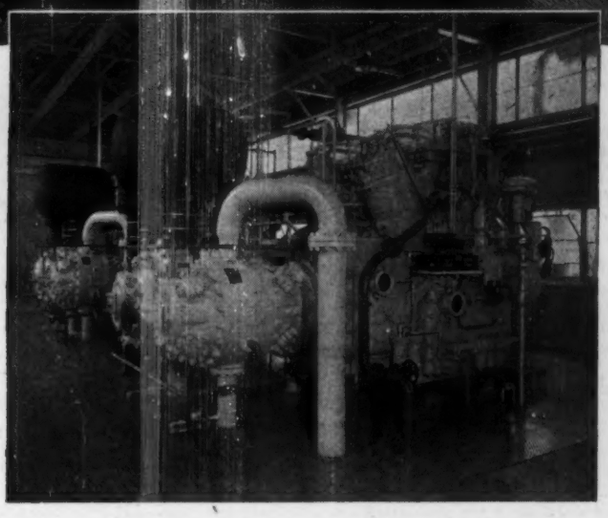
11. Quick Connecting Utility Outlet

WHEN quantities of water are required, as for fire control, it is needed in a hurry. No one must waste time hunting for gaskets, or wire brushes to clean the face of the companion flange attached to the pipe outlet. At the most logical point for immediate use, the pipe line is laid with the terminal connection where it can be reached safely and without loss of time. The end is fitted with a half bolted flange, companion to the type attached to the equipment which may be used instantly. The end of the line is supported on the fire wall with a pedestal bracket solidly fastened to the wall with lag screws. The companion flange is complete, supplied with a composition ring gasket all in readiness for quick connection. So that the elements will not damage the face of the flange or the gasket, the coupling face is covered with a steel lid.



The seven GMV compressors installed in the Styrene Plant of The Dow Chemical Company are here shown from the compressor cylinder side. The fourth and fifth GMV's are eight-cylinder, 800-hp feed gas units. Compressors six and seven in this interesting line-up are GMV four-cylinder ethylene units.

GMV "angles" For the Products of Tomorrow



Close-up of the two GMV-4 400-hp ethylene units showing compressor cylinders, piping and control equipment.

At The Dow Chemical Company's Styrene Plant, Los Angeles, California, seven modern GMV compressors help produce monomeric styrene as well as several other products, all having important peacetime applications.

As always, selection of compact, rugged GMV's made possible an economical and highly practical compressor setup. For example, fast, positive response to sensitive control instruments has been highly developed in the GMV, making it particularly desirable for modern processing requirements. Responsiveness is only one of the many phases of operation in which the GMV excels. Likewise there are exclusive features of design and construction that have helped earn for this modern 400, 600, 800 and 1000 hp compressor a reputation for truly exceptional service and performance.

The GMV Bulletin, 48 pages of data and interesting information, will be mailed in response to your request.

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Oil Demand One Fourth Greater Than in 1941

L. J. LOGAN

OPERATIONS during the first half all conditions oils are highly essential, and expecting temporary minor interruptions, the trend is one of ever-increasing consumption. Growth of population alone assures some increase, and wider utilization of machinery accentuates the increases. War and the end of war have caused readjustments but have not changed the general trend toward ever-expanding use of oils. Consumption is heading toward new record levels and already approaches them, following the early postwar readjustments.

In the first six months of 1946, the total demand for all oils amounted to 955,129,000 barrels, compared with 1,009,153,000 barrels used in the corresponding months of 1945, which were the closing months of the war, bringing peak wartime use. These figures indicate daily average total demand for all of 1946 exceeded virtually all expectations, and activity proceeded at high levels as the latter half of the year commenced.

In these unexpectedly high levels of operations there has been demonstrated once more the remarkable immunity of petroleum consumption to the periodic changes in general conditions. Under oils was 5,277,000 barrels in the first half of 1946, a decrease of 5.4 percent from the 5,575,000 daily of the first half of 1945 but an increase of 25.7 percent over the 4,197,000 barrels daily recorded for January-June, 1941, the last prewar year for the United States. This large increase above prewar consumption exceeded practically all earlier expectations.

Domestic Use Above Forecasts

A noteworthy feature of this year's demand for petroleum is the fact that domestic consumption is stronger than expected while exports are less than forecast. Total domestic demand for all oils averaged 4,836,000 barrels daily in the first six months of 1946, only 2.4 percent less than the 4,955,000 daily of the like months of 1945 and 22.7 percent more than the 3,943,000 daily recorded for the initial half of 1941. Exports of 441,000 daily were 29 percent less than the 620,000 daily last year and 73.1 percent more than the 255,000 daily of the first half of 1941. Crude oil exports averaged 82,000 barrels daily this year against 75,000 daily last year and 88,000 daily in 1941. Exports of refined products averaged 359,000 barrels daily for January-June 1946, compared with 545,000 in 1945 and 167,000 daily in the first half of 1941.

Stocks of Crude Petroleum in U. S. by Grades, at End of June

Based on Weekly Reports of U. S. Bureau of Mines

(THOUSANDS OF BARRELS)

GRADE OR ORIGIN	June 28, 1941	June 30, 1945	June 29, 1946	Change, 1941-1946	Change, 1945-1946
Pennsylvania Grade	4,297	2,114	2,493	— 1,804	+ 379
Other Appalachian	1,420	1,304	1,539	+ 119	+ 235
Lima-Michigan	1,020	975	1,064	+ 44	+ 89
Illinois-Indiana	20,246	12,479	17,747	— 2,499	+ 5,268
Arkansas	2,745	2,786	2,649	— 96	— 137
Kansas	8,755	9,277	8,746	— 9	— 531
Louisiana	12,439	13,915	10,824	— 1,615	— 3,091
Northern	4,424	3,562	2,751	— 1,673	— 1,077
Gulf Coast	8,015	10,353	8,073	+ 58	— 2,280
Mississippi	1,507	1,256	2,161	+ 654	+ 905
New Mexico	7,203	5,953	5,936	— 1,267	— 17
Oklahoma	57,158	31,261	33,825	—23,333	+ 2,564
Texas	88,991	110,848	104,605	+15,614	— 6,243
East Texas	22,698	19,323	16,953	— 5,745	— 2,370
West Texas	16,557	31,687	36,034	+19,477	+ 4,347
Gulf Texas	25,596	31,353	27,932	+ 2,336	— 3,441
Other Texas	24,140	28,485	23,686	— 454	— 4,799
Panhandle	.....	4,924	4,326	+ 4,326	— 598
North	.....	7,581	6,338	+ 6,338	— 1,243
South	.....	7,381	5,210	+ 5,210	— 2,171
Other	.....	8,599	7,812	+ 7,812	— 787
Rocky Mountain	15,928	6,642	8,381	— 7,547	+ 1,739
California	35,125	18,813	20,478	—14,647	+ 1,665
Foreign	2,565	3,158	3,435	+ 870	+ 277
Total Gasoline Bearing in U. S.	259,399	220,781	223,883	—35,516	+ 3,102
Heavy in California	10,716	4,940	5,004	— 5,712	+ 64
Total in U. S.	270,115	225,721	228,887	—41,228	+ 3,166

In supplying the unexpectedly high demand for oils this year, there has been some increase in imports above receipts in former years while domestic production has been materially greater than expected. Imports are limited mainly to heavy crude oils and residual fuel oils, and these foreign oils have been urgently needed this year in meeting the large requirements of fuel oils by the Navy and merchant vessels. Imports of residual fuel oil and miscellaneous other refined products averaged 127,000 barrels daily in this year's first half, compared with 124,000 daily in 1945 and 116,000 daily in 1941. Imports of crude show much sharper increases, having averaged 227,000 daily in 1946 against 174,000 in 1945 and 122,000 in 1941.

Domestic production includes natural gasoline and benzol besides crude petroleum, but output of the first two is not materially different from last year. Natural gasoline production averaged 307,000 barrels daily from January-June 1946, against 310,000 daily in those months of 1945 and 207,000 daily in 1941. Benzol production of 8000 daily compared with 8000 in 1945 and 9000 in 1941. U. S. production of crude averaged 4,678,000 barrels daily in the first half of 1946, a decrease of only 2.7 percent from the 4,806,000 daily in January-June 1945 and 27.1 percent more than the 3,620,000 daily of 1941's first six months. For this year it now is indicated that domestic production will average more than 300,000 barrels per day in excess of earlier forecasts.

Stocks Increased Moderately

It is true that the relatively high rates of crude production have resulted in some accumulation of crude and products in storage, with new supply somewhat exceeding current consumption. However, these accumulations have not been excessive. On the contrary, they have been generally justified, because of the extremely low levels to which inventories were drawn under wartime necessity. The accumulations in storage have been undesirable only as regards individual products, as gasoline storage was increased more than needed, while there have been at times deficiencies of fuel oils. These maladjustments have been due mainly to continued government price fixing which has not been such as to permit balancing of production of individual products with demand for those products.

In the first six months of 1946 total stocks of all oils were increased 12,530,000 barrels, an average of 69,000 barrels daily, compared with withdrawals of 154,000 daily in 1945 and 63,000 daily in 1941. Stocks of crude petroleum were in-

Production, Imports, Stocks, Exports, and Domestic Demand, First Half of Year

Figures from U. S. Bureau of Mines except second quarter of 1946 based on American Petroleum Institute weekly reports and Bureau of Mines forecasts.

(THOUSANDS OF BARRELS)

ITEM	First Half 1941	First Half 1945	First Half 1946	% Diff. 1941-1946	% Diff. 1945-1946
ALL OILS					
Domestic Production, Total	705,237	927,367	903,659	+ 28.1	— 2.6
(Daily Average)	3,896	5,124	4,933	+ 28.1	— 2.6
Crude Petroleum	666,098	869,802	846,638	+ 27.1	— 2.7
(Daily Average)	3,680	4,806	4,678	+ 27.1	— 2.7
Natural Gasoline	37,403	56,125	55,581	+ 48.6	— 1.0
(Daily Average)	207	310	307	+ 48.6	— 1.0
Benzol	1,736	1,440	1,440	— 17.1	.....
(Daily Average)	9	8	8	— 17.1	.....
Imports, Total	43,059	53,871	64,000	+ 48.6	+ 18.8
(Daily Average)	237	298	354	+ 48.6	+ 18.8
Crude Petroleum	22,014	31,497	41,000	+ 86.2	+ 30.2
(Daily Average)	122	174	227	+ 86.2	+ 30.2
Refined Products	21,045	22,374	23,000	+ 9.3	+ 2.8
(Daily Average)	116	124	127	+ 9.3	+ 2.8
Changes in Stocks, All Oils	—11,407	—27,915	+12,530	.....	.....
(Daily Average)	—63	—154	+69	.....	.....
Stocks, Beginning of Period	563,277	477,089	463,579	— 17.7	— 2.8
Refinable Crude	264,709	220,862	218,763	— 17.4	— 1.0
Heavy Crude in California	11,906	6,107	4,496	— 62.2	— 26.4
Refined Products	280,958	245,868	235,998	— 16.0	— 4.0
Natural Gasoline	5,704	4,252	4,322	— 24.2	+ 1.6
Stocks, End of Period	551,870	449,174	476,109	— 13.7	+ 6.0
(Days' Supply)	131	81	90	— 31.3	+ 11.1
Refinable Crude	259,695	218,218	223,883	— 13.8	+ 2.6
Heavy Crude in California	10,711	5,044	5,004	— 53.3	— 0.8
Refined Products	275,229	221,189	240,522	— 12.6	+ 8.7
Natural Gasoline	6,235	4,723	6,700	+ 7.5	+ 4.9
Demand, Total	759,703	1,009,153	955,129	+ 25.7	— 5.4
(Daily Average)	4,197	5,575	5,277	+ 25.7	— 5.4
Exports, Total	46,110	112,318	79,800	+ 73.1	— 29.0
(Daily Average)	255	620	441	+ 73.1	— 29.0
Crude Petroleum, Total	15,896	13,660	14,800	— 6.9	+ 8.3
(Daily Avdrage)	88	75	82	— 6.9	+ 8.3
Refined Products, Total	30,214	98,658	65,000	+ 115.1	— 34.1
(Daily Average)	167	545	359	+ 115.1	— 34.1
Domestic Demand, Total	713,593	896,835	875,329	+ 22.7	— 2.4
(Daily Average)	3,943	4,955	4,836	+ 22.7	— 2.4
CRUDE PETROLEUM					
Supply:					
Domestic Production, Total	666,098	869,802	846,638	+ 27.1	— 2.7
(Daily Average)	3,680	4,805	4,678	+ 27.1	— 2.7
Imports, Total	22,014	31,497	41,000	+ 86.2	+ 30.2
(Daily Average)	122	174	227	+ 86.2	+ 30.2
Change in Stocks (Incl. Heavy Crude in Calif.)	—6,209	—3,508	+5,628	.....	.....
(Daily Average)	—34	—19	+31	.....	.....
Stocks, Beginning of Period	276,615	226,770	223,259	— 19.3	— 1.5
Stocks, End of Period	270,406	223,262	228,887	— 15.4	+ 2.5
(Days' Supply)	70	45	47	— 32.9	+ 4.4
Supply, Total	694,321	904,807	882,010	+ 27.0	— 2.5
(Daily Average)	3,836	4,999	4,873	+ 27.0	— 2.5
Demand:					
Runs to Stills, Total	668,663	871,436	848,520	+ 26.9	— 2.6
(Daily Average)	3,694	4,815	4,688	+ 26.9	— 2.6
Domestic Crude	646,056	840,694	808,120	+ 25.1	— 3.9
(Daily Average)	3,569	4,645	4,465	+ 25.1	— 3.9
Foreign Crude	22,607	30,742	40,400	+ 78.7	+ 31.4
(Daily Average)	125	170	223	+ 78.7	+ 31.4
Exports, Total	15,896	13,660	14,800	— 6.9	+ 8.3
(Daily Average)	88	75	82	— 6.9	+ 8.3
Transfers to Fuel Oil Stocks	6,022	12,818	10,652	+ 76.9	— 16.9
(Daily Average)	33	71	59	+ 76.9	— 16.9
Distillate Fuel Oil	1,220	1,568	1,436	+ 17.7	— 8.4
Residual Fuel Oil	4,802	11,250	9,216	+ 91.9	— 18.1
Used as Fuel, and Losses	3,740	6,893	8,038	+ 114.9	+ 16.6
(Daily Average)	21	38	44	+ 114.9	+ 16.6
Demand, Total	694,321	904,807	882,010	+ 27.0	— 2.5
(Daily Average)	3,836	4,999	4,873	+ 27.0	— 2.5
MOTOR FUEL					
Production, Total	328,014	400,624	370,535	+ 13.1	— 7.4
(Daily Average)	1,812	2,213	2,049	+ 13.1	— 7.4
Refinery Gasoline, Total	291,968	352,279	326,212	+ 11.7	— 7.4
(Daily Average)	1,613	1,946	1,802	+ 11.7	— 7.4
(Yield from Crude)	43.7	40.4	38.4	.....	.....
Cracked	159,356	203,039	.....	.....	.....
Straight Run	132,612	149,240	.....	.....	.....
Natural Gasoline, etc.	37,403	56,125	55,581	+ 48.6	— 1.0
(Daily Average)	207	310	307	+ 48.6	— 1.0
Less sales of L. P. G.	3,093	8,759	11,873	+ 283.9	+ 35.6
Less transfers cycle prods.	.....	461	525	.....	+ 13.9
Benzol	1,736	1,440	1,440	— 17.1	.....
Imports, Total	.....	1,190	.....	.....	.....
(Daily Average)	.....	7	.....	.....	.....
Change in Stocks	—154	+938	—3,387	.....	.....
(Daily Average)	—1	+5	—19	.....	.....
Stocks, Beginning of Period	88,800	77,874	93,682	+ 5.5	+ 20.3
Finished Gasoline	83,310	73,622	89,360	+ 7.3	+ 21.4
Natural Gasoline	5,490	4,252	4,322	— 22.6	+ 1.6
Stocks, End of Period	88,646	78,812	90,295	+ 1.9	+ 14.6
(Days' Supply)	50	36	44	— 12.0	+ 22.2
Finished Gasoline	82,411	74,089	83,595	+ 1.4	+ 12.9
Natural Gasoline	6,235	4,723	6,700	+ 7.5	+ 41.9
Demand, Total	323,016	401,075	374,222	+ 15.9	— 6.7
(Daily Average)	1,785	2,216	2,068	+ 15.9	— 6.7
Exports, Total	9,410	64,916	31,000	+ 229.4	— 52.2
(Daily Average)	52	359	171	+ 229.4	— 52.2
Domestic Demand	313,606	336,159	343,222	+ 9.4	+ 2.1
(Daily Average)	1,733	1,857	1,896	+ 9.4	+ 2.1
KEROSINE					
Production, Total	35,901	39,003	55,203	+ 53.8	+ 41.5
(Daily Average)	198	215	305	+ 53.8	+ 41.5
Percent Yield from Crude	5.4	4.5	6.5	.....	.....
Imports, Total	43	.....	.....	.....	.....
(Daily Average)	.....	.....	.....	.....	.....
Change in Stocks	+97	—1,551	+3,460	.....	.....
(Daily Average)	+1	—8	+19	.....	.....
Stocks, Beginning of Period	9,512	11,150	10,421	+ 9.6	— 6.5
Stocks, End of Period	9,609	9,599	13,881	+ 44.5	+ 44.6
(Days' Supply)	49	43	49	.....	+ 14.0
Demand, Total	35,847	40,554	51,743	+ 44.3	+ 27.6
(Daily Average)	198	224	286	+ 44.3	+ 27.6
Exports, Total	802	2,622	2,715	+ 238.5	+ 3.5
(Daily Average)	4	14	15	+ 238.5	+ 3.5
Domestic Demand	35,045	37,932	49,028	+ 39.9	+ 29.3
(Daily Average)	194	210	271	+ 39.9	+ 29.3
DISTILLATE FUEL OIL					
Production, Total	92,072	126,032	142,640	+ 54.9	+ 13.2
(Daily Average)	509	696	788	+ 54.9	+ 13.2
Percent Yield from Crude	13.8	14.5	16.8	.....	.....
Transfers from Crude	1,220	1,568	1,436	+ 17.7	— 8.4
(Daily Average)	7	9	8	+ 17.7	— 8.4
Imports, Total	1,887	2,695	3,000	+ 59.0	+ 11.3
(Daily Average)	10	15	17	+ 59.0	+ 11.3
Change in Stocks	—4,637	—5,893	+1,984	.....	.....
(Daily Average)	—26	—33	+11	.....	.....
Stocks, Beginning of Period	42,911	38,333	35,778	— 16.6	— 6.7
Stocks, End of Period	38,274	32,440	37,762	— 1.3	+ 16.4
(Days' Supply)	69	43	47	— 30.4	+ 9.3
Demand, Total	99,816	136,188	145,092	+ 45.4	+ 6.5
(Daily Average)	551	752	802	+ 45.4	+ 6.5
Exports, Total	6,826	19,267	16,000	+ 134.4	— 17.0
(Daily Average)	38	106	88	+ 134.4	— 17.0
Domestic Demand	92,990	116,921	129,092	+ 38.8	+ 10.4
(Daily Average	514	646	713	+ 38.8	+ 10.4
RESIDUAL FUEL OIL					
Production, Total	164,125	239,230	225,256	+ 37.2	— 5.8
(Daily Average)	907	1,322	1,245	+ 37.2	— 5.8
Percent Yield from Crude	24.5	27.5	26.5	.....	.....
Transfers from Crude	4,802	11,250	9,216	+ 91.9	— 18.1
(Daily Average)	27	62	51	+ 91.9	— 18.1
Imports, Total	17,021	18,123	20,000	+ 17.5	+ 10.4
(Daily Average)	94	100	110	+ 17.5	+ 10.4
Change in Stocks	—8,078	—14,777	+4,388	.....	.....
(Daily Average)	—45	—82	+24	.....	.....
Stocks, Beginning of Period	88,026	50,383	37,158	— 57.8	— 26.2
Stocks, End of Period	79,948	35,606	41,546	— 48.0	+ 16.7
(Days' Supply)	74	23	30	— 59.5	+ 30.4
Demand, Total	194,026	283,380	250,084	+ 28.9	— 11.7
(Daily Average)	1,072	1,566	1,382	+ 28.9	— 11.7
Exports, Total	6,773	6,617	5,300	— 21.7	— 19.9
(Daily Average)	37	37	29	— 21.7	— 19.9
Domestic Demand	187,253	276,763	244,784	+ 30.7	— 11.6
(Daily Average)	1,035	1,529	1,352	+ 30.7	— 11.6
LUBRICATING OILS					
Production, Total	18,333	21,320	21,616	+ 17.9	+ 1.4
(Daily Average)	101	118	119	+ 17.9	+ 1.4
Percent Yield from Crude	2.7	2.4	2.5	.....	.....
Change in Stocks	—1,414	—1,045	+227	.....	.....
(Daily Average)	—8	—6	+1	.....	.....
Stocks, Beginning of Period	8,767	7,815	7,773	— 11.3	— 0.5
Stocks, End of Period	7,353	6,770	8,000	+ 8.8	+ 18.2
(Days' Supply)	67	55	68	+ 1.5	+ 23.6
Demand, Total	19,747	22,365	21,389	+ 8.3	— 4.4
(Daily Average)	109	124	118	+ 8.3	— 4.4
Exports, Total	4,548	3,470	6,275	+ 38.0	+ 80.8
(Daily Average)	25	19	35	+ 38.0	+ 80.8
Domestic Demand	15,199	18,895	15,114	— 0.6	— 20.0
(Daily Average)	84	104	84	— 0.6	— 20.0

creased 5,628,000 barrels in the first half of this year, an average of 31,000 barrels daily, compared with increases of 19,000 daily last year and 34,000 daily in 1941. This accumulation of crude in storage was quite satisfactory, as inventories have been generally very close to minimum working stock levels. The 228,887,000 barrels of crude in storage at the end of June 1946 included only 223,883,000 barrels of refinable crude and 5,004,000 barrels of heavy crude in California and represented only 47 days' supply at the rate of consumption in the first half of this year. Total crude stocks of 223,262,000 barrels at midyear 1945 represented 45 days' supply. Those of 270,406,000 barrels June 30, 1941, represented 70 days' supply, although much excess of crude then was held in California.

Motor Fuel Demand High

Today's situation on stocks is generally desirable as regards most of the products as well as crude. The danger of overstocking has been limited to motor fuel, but even that product is not in real surplus. Stocks of motor fuel totaled 90,295,000 barrels at the end of June, and represented 44 days' supply at the rate of use this year's first six months. As a factor in firm markets, they compared unfavorably with the 78,812,000 barrels or 36 days' supply held a year previously but favorably with the 88,646,000 barrels or 50 days' supply held at midyear 1941. Total demand for motor fuel averaged 2,068,000 barrels daily in January-June 1946, down 6.7 percent from the 2,216,000 daily last year but 15.9 percent above the 1,785,000 barrels daily of demand in the first half of 1941. Exports are only half as great this year as they were last year in averaging 171,000 barrels daily against 359,000, but they are more than three times the 52,000 daily exported in January-June 1941. Domestic demand for motor fuel has been much higher than expected. It averaged 1,896,000 barrels daily for the first six months, up 2.1 percent from the 1,857,000 daily last year and 9.4 percent above the 1,733,000 daily in January-June 1941. Aviation and other non-automotive uses account for the increase above prewar, and these uses plus lifting of rationing have more than offset the postwar decline in military requirements. Thus reduced exports are wholly responsible for failure of total demand to run as high this year as it did last year.

Kerosine Stocks

Kerosine stocks of 13,881,000 barrels at midyear represented 49 days' supply and compared with 9,599,000 barrels or 43 days' supply a year previously and 9,609,000 barrels or 49 days' supply at midyear 1941. Total demand averaged 286,000 barrels daily in the first six months, up 27.6 percent from the 224,000 daily last year and 44.3 percent above the 198,000 daily of 1941. Exports have been slightly above last year, and domestic demand of 271,000 barrels daily was 29.3 percent above the 210,000 daily in 1945 and 39.9 percent above the 194,000 daily used in the first half of 1941.

Distillate fuel oil stocks have been made more adequate than a year ago but are still subnormal. The 37,762,000 barrels held at the end of June this year represented 47 days' supply at this year's rate of consumption and compared with 32,440,000 barrels or 43 days' supply held a year previously and 38,274,000 barrels or 69 days' supply on hand at midyear 1941, since which time demand has increased greatly. Total demand for distillate fuel averaged 802,000 barrels daily in January-June 1946, up 6.5 percent from the 752,000 daily last year and 45.4 percent above the 551,000 daily in 1941. Exports averaged 88,000 barrels daily this year, down 17 percent from the 106,000 daily last year but more than double the shipments of 38,000 daily in January-June 1941. Domestic demand of 713,000 barrels daily in this year's first half was 10.4 percent above that of 646,000 daily in the like period last year and 38.8 percent above the 514,000 daily of 1941.

Residual Fuel Oil

Stocks of residual fuel oil also are less short than a year ago but not too large. They totaled 41,546,000 barrels June 29, 1946, equivalent to 30 days' supply at this year's consumption rate. On June 30 last year the stocks totaled 35,606,000 barrels or 23 days' supply. At midyear 1941 they amounted to 79,948,000 barrels, equal to 74 days' supply. The large reduction since then reflects mainly the wartime liquidation of surplus stocks in California, as in the case of crude stocks. As expected, demand for residual fuel oil has diminished since the end of war, but the decline has been less than forecast. Total demand averaged 1,382,000 barrels daily in the first half of this year, 11.7 percent less than the 1,566,000 daily last year but 28.9 percent more than the 1,072,000 daily used in the first half of 1941. Exports averaged 29,000 barrels daily, compared with 37,000 daily in both 1945 and 1941. Domestic demand averaged 1,352,000 barrels daily, down 11.6 percent from the 1,529,000 daily in 1945 but 30.7 percent above the 1,035,000 daily of 1941. Continued activity of the Navy and the merchant ships explains the relatively high usage of residual fuel this year.

Stocks of lubricating oils have tended to increase this year but are about normal in relation to demand. They are estimated at 8 million barrels at the end of June this year, equivalent to 68 days' supply. Total demand for lubricants averaged about 118,000 barrels daily in this year's first half, down 4.4 percent from the 124,000 daily used in last year's first six months but 8.3 percent above the 109,000 daily required in 1941. Increased exports have almost compensated for the decrease this year in domestic demand. Exports averaged about 35,000 barrels daily, compared with 19,000 daily in 1945 and 25,000 daily in 1941. Domestic demand averaged 84,000 daily, down 20 percent from the 104,000 daily of 1945 but the same as in 1941.

Crude Production Lower

As generally foreseen, the cutback in domestic crude oil production after the end of the war was made largely by lowering output in Texas. While U. S. production in the first half of 1946 was

U. S. Crude Runs to Stills and Percent of Refinery Capacity Used by Districts, June, 1946, and First 6 Months of 1946

Runs from Bureau of Mines, except second quarter of 1946 from American Petroleum Institute. Capacities from American Petroleum Institute.
(THOUSANDS OF BARRELS)

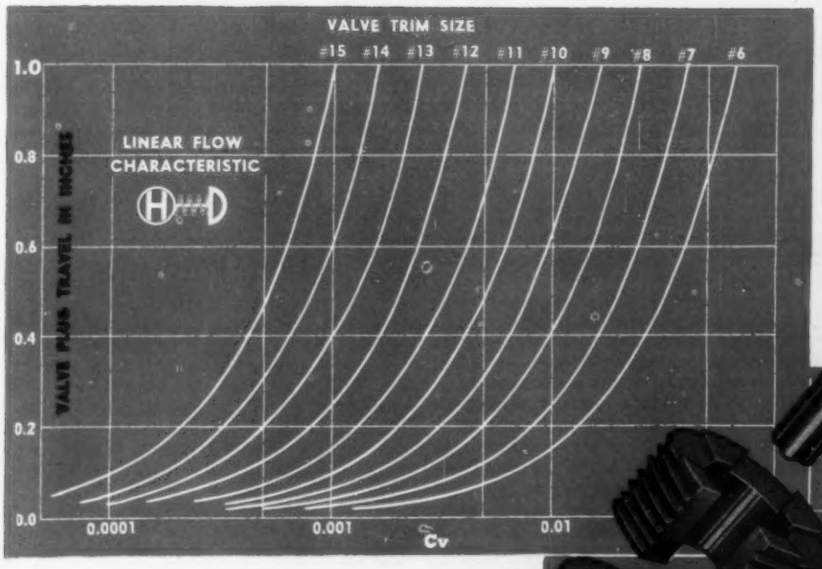
REFINING DISTRICT	CRUDE RUNS IN JUNE: Total Amount Run				CRUDE RUNS IN JUNE: Daily Average Run			REFINING CAPACITY IN USE, JUNE: Daily Capacity			REFINING CAPACITY IN USE, JUNE: Percent Capacity Used			TOTAL AMOUNT OF CRUDE RUN TO STILLS, FIRST 6 MONTHS			
	June, 1941	June, 1945	June, 1946	% Diff. '45-'46	June, 1941	June, 1945	June, 1946	June, 1941	June, 1945	June, 1946	June, 1941	June, 1945	June, 1946	Jan. to June, 1941	Jan. to June, 1945	Jan. to June, 1946	% Diff. '45-'46
East Coast	16,955	22,155	23,172	+ 4.6	565	738	772	643	791	839	87.9	93.3	92.0	101,988	132,839	138,263	+ 4.1
Appalachian	4,491	4,821	4,561	— 5.4	150	161	152	156	196	205	96.2	82.1	74.1	25,924	28,944	27,510	— 5.0
District No. 1	.....	3,131	2,889	— 7.7	.....	105	96	.....	146	143	.....	71.9	67.1	.....	18,068	17,380	— 3.8
District No. 2	.....	1,690	1,672	— 1.1	.....	56	56	.....	50	62	.....	112.0	90.3	.....	10,876	10,130	— 6.9
Illinois, Indiana, Kentucky	21,225	23,080	22,870	— 0.9	707	769	762	743	857	870	95.2	89.7	87.6	118,707	141,108	133,831	— 5.2
Oklahoma, Kansas, Missouri	10,831	11,943	11,494	— 3.8	361	398	383	420	469	470	86.0	84.9	81.5	60,578	69,926	67,892	— 2.9
Texas Inland	5,551	7,298	6,693	— 8.3	185	243	223	280	330	331	66.1	73.6	67.4	32,102	43,496	38,343	—11.8
Texas Gulf	28,482	36,524	36,209	— 0.9	950	1,217	1,207	1,071	1,237	1,226	88.7	98.4	98.5	171,374	210,316	209,788	— 0.3
Louisiana Gulf	4,448	8,315	10,133	+21.9	148	277	338	164	260	322	90.2	106.5	105.0	24,859	46,433	57,406	+23.6
Arkansas and Louisiana Inland	2,124	2,596	1,621	—37.6	71	87	54	101	126	126	70.3	69.0	42.9	13,524	14,531	10,283	—29.2
Rocky Mountain	2,924	4,338	4,277	— 1.4	97	145	143	121	172	178	80.2	84.3	80.3	15,805	23,291	23,459	+ 0.7
District No. 3	.....	387	337	—12.9	.....	13	11	.....	13	13	.....	100.0	84.6	.....	2,226	2,017	— 9.4
District No. 4	.....	3,951	3,940	— 0.3	.....	132	132	.....	159	165	.....	83.0	80.0	.....	21,065	21,442	+ 1.8
California	18,904	28,612	23,879	—16.5	630	954	796	836	994	994	75.3	96.0	80.1	103,802	160,552	141,745	—11.7
Total United States	115,935	149,652	144,909	— 3.2	3,864	4,989	4,830	4,535	5,432	5,561	85.2	91.8	86.9	668,663	871,436	848,520	— 2.6

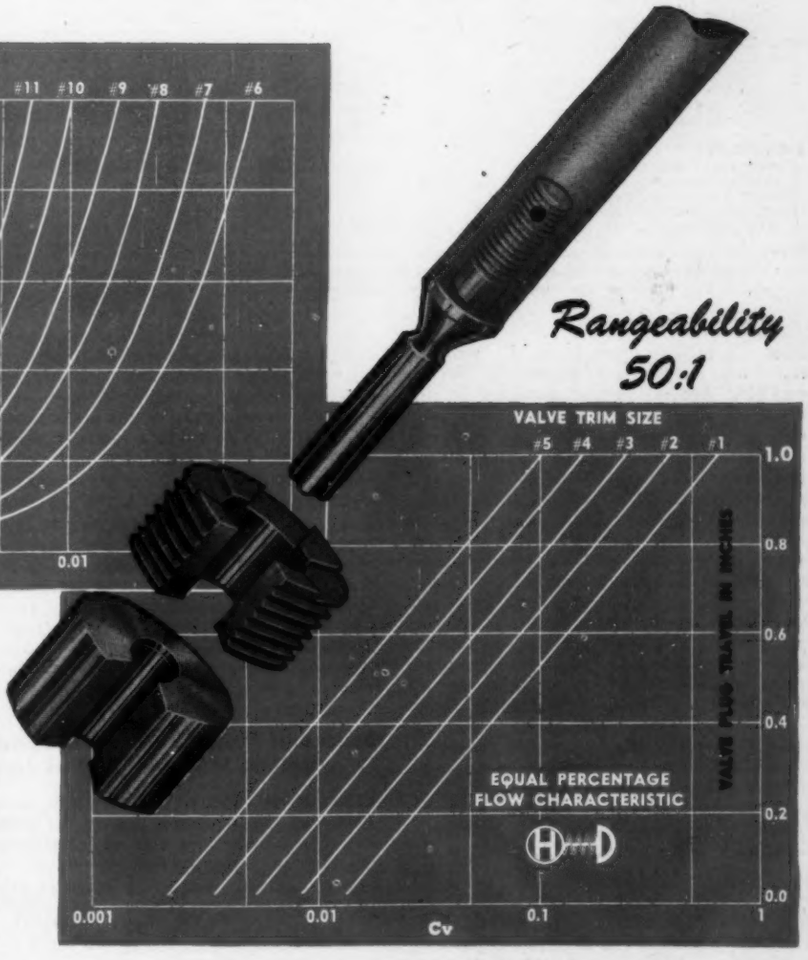
AUTOMATIC CONTROL EQUIPMENT

ENGINEERED DESIGN BY **HAMMEL-DAHL**

The "C_vs" of the Spline Type Plugs mean "cc" flow control

The flow coefficient "Cv" at one inch of lift is equal to the maximum rate of flow in GPM of water at one psi pressure drop across the diaphragm control valve.





Rangeability 50:1

TRIM SIZE	Cv	TRIM SIZE	Cv	TRIM SIZE	Cv
#1	0.63	#6	0.063	#11	0.0063
#2	0.40	#7	0.040	#12	0.0040
#3	0.25	#8	0.025	#13	0.0025
#4	0.16	#9	0.016	#14	0.0016
#5	0.10	#10	0.010	#15	0.0010

"Fifteen" **SPLINE TYPE SEAT GUIDED PLUGS are INTERCHANGEABLE in 1/2, 3/4 and 1" Microflow Bar Stock Bodies. Stellite J metal is standard trim. Specific flow test calibrations available on request.**

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Refinery Production of Major Products and Percent Yield from Crude Run at U. S. Refineries

Results in June and first 6 months, 1946, compared with those in like periods last year and in 1941, last pre-war year for U. S. All data from U. S. Bureau of Mines except second quarter of 1946 based on weekly reports of American Petroleum Institute.

(THOUSANDS OF BARRELS)

ITEM	1941	1945	1946	% Diff. 1941-46	% Diff. 1945-46
*GASOLINE:					
Production, June	55,136	64,972	61,258	+ 11.1	— 5.7
(Daily Average)	1,838	2,166	2,042	+ 11.1	— 5.7
Percent Yield from Crude	44.5	39.4	39.1	.....	.....
Production, January-June	313,297	388,510	354,191	+ 13.1	— 8.8
(Daily Average)	1,731	2,147	1,957	+ 13.1	— 8.8
KEROSINE:					
Production, June	5,218	6,337	8,474	+ 62.4	+ 33.7
(Daily Average)	174	211	282	+ 62.4	+ 33.7
Percent Yield from Crude	4.5	4.2	5.8	.....	.....
Production, January-June	35,901	39,003	55,203	+ 53.8	+ 41.5
(Daily Average)	198	215	305	+ 53.8	+ 41.5
DISTILLATE FUEL OIL:					
Production, June	14,697	21,891	23,385	+ 59.1	+ 6.8
(Daily Average)	490	730	780	+ 59.1	+ 6.8
Percent Yield from Crude	12.7	14.6	16.1	.....	.....
Production, January-June	92,011	126,032	142,640	+ 55.0	+ 13.2
(Daily Average)	508	696	788	+ 55.0	+ 13.2
RESIDUAL FUEL OIL:					
Production, June	28,255	40,527	38,010	+ 34.5	— 6.2
(Daily Average)	942	1,351	1,267	+ 34.5	— 6.2
Percent Yield from Crude	24.4	27.1	26.2	.....	.....
Production, January-June	165,753	239,230	225,256	+ 35.9	— 5.8
(Daily Average)	916	1,321	1,245	+ 35.9	— 5.8
LUBRICANTS:					
Production, June	3,520	3,567	3,768	+ 7.0	+ 5.6
(Daily Average)	117	119	126	+ 7.0	+ 5.6
Percent Yield from Crude	3.0	2.4	2.6	.....	.....
Production, January-June	18,333	21,320	21,616	+ 17.9	+ 1.4
(Daily Average)	101	118	119	+ 17.9	+ 1.4

* Production includes straight run, cracked, and natural blended at refineries. Yield indicates percent of crude runs made into straight run and cracked gasoline.

about 23 million barrels or 2.7 percent less than in the corresponding period of 1945, Texas output showed a decrease of 19½ million barrels or 5 percent. The next most important decrease was that of 11 million barrels or 6.5 percent for California. Kansas showed a decrease of approximately 2 million barrels or 4.6 percent, and New Mexico about 1 million barrels or 6.4 percent. Decreases of less than 1 million barrels occurred in Arkansas, down 5.2 percent, Michigan down 3.4 percent, Montana down 4.2 percent and Nebraska down 13.8 percent. Production has run higher this year than last year in all other states, representing a good majority of the producing states. Alabama, Colorado, and Florida are each producing more than twice their output a year ago, through benefit of discovery of new reserves. Increases in other states and districts have been as follows: Illinois 7/10 of 1 percent, Indiana 42.7 percent, Kentucky 9.8 percent, Louisiana 5.7 percent, North Louisiana 25.5 percent, South Louisiana 1.4 percent, Mississippi 13.7 percent, Missouri 47.6 percent, New York 6.6 percent, Oklahoma 1.2 percent, Pennsylvania 2.0 percent, West Virginia 5.8 percent, Wyoming 4.8 percent. While all other Texas districts showed decreases, there were increases of 5.1 percent for North Texas and 4.6 percent for West Texas.

Refinery runs of domestic and foreign crude oil at U. S. plants totaled 848,520,000 barrels in the first half of 1946, an average of 4,688,000 barrels daily. As in the first six months of 1945 and 1941, total runs to stills conformed very closely with domestic production of crude with the equivalent of requirements of crude for other purposes supplied by imports; these other demands being for export, transferring to fuel oil stocks for use without refining, and to compensate for refinery losses, while in 1946 some crude went into storage. In the first half of this year, the 4,688,000 barrels daily average of runs to stills was 10,000 a day above the domestic production of 4,678,000 barrels daily, the same difference as in 1945's first half and comparing with an excess of 14,000 daily above domestic production in the first six months of 1941. While domestic production was supplemented in the first half of this year by imports of 227,000 barrels daily, almost the equivalent of the imports was required by the exports of 82,000 daily, transfers to fuel oil stocks of 59,000 daily, use direct as fuel and losses of 44,000 daily, and additions to storage averaging 31,000 barrels daily. Imported crude was used this year strictly for the balancing of operations, virtually all received having been charged to stills and practically none having been added to storage.

The refinery runs of 4,688,000 barrels daily in January-June 1946 were 2.6 percent below the runs of 4,815,000 daily in the like months of 1945 but 26.9 percent above the runs of 3,694,000 daily in the like period of 1941.

Through the reduction this year in runs to stills, a more normal and satisfactory load has been placed on refinery capacity, in contrast with wartime crowding of capacity which did not always permit needed repairs. This situation has been improved a little also by limited further increase in total capacity of U. S. plants, which were rated at 5,561,000 barrels daily June 30, 1946, compared with 5,432,000 daily a year previously and 4,535,000 daily at mid-year 1941. During June of this year, plants were operated at 86.9 percent of rated capacity, compared with 91.8 percent utilization of capacity in June last year and runs at 85.2 percent of existing capacity in June of 1941.

While U. S. runs to stills were 2.6 percent under last year for the first six months of 1946, several refining districts showed increases, including those of 4.1 percent for the East Coast, 23.6 percent for the Louisiana Gulf Coast, and 1.8 percent for Rocky Mountain District 4 (outside New Mexico), in each of which districts capacity is larger than a year ago. Much of the decrease from last year occurred in California, where a reduction of 11.7 percent brought the amount of crude charged to stills down to 141,745,000 barrels from 160,552,000 barrels processed in the first half of 1945. The Appalachian districts showed a 5 percent decrease in runs, Illinois-Indiana-Kentucky 5.2 percent, Oklahoma-Kansas-Missouri 2.9 percent, Inland Texas 11.8 percent, the Texas Gulf Coast 3/10 of 1 percent, Arkansas 29.2 percent, and New Mexico 9.4 percent.

Stocks of Major Petroleum Products Held by Refining Companies in the United States at End of June, Compared with 1941 and 1945

Stocks at refineries, at bulk terminals, in transit, and in pipe lines. Data for 1941 and 1945 from Bureau of Mines monthly reports; for 1946 from weekly report of American Petroleum Institute.

(THOUSANDS OF BARRELS)

DISTRICT	FINISHED AND UNFINISHED GASOLINE Stocks End of June			KEROSINE Stocks End of June			GASOIL AND DISTILLATE FUEL Stocks End of June			RESIDUAL FUEL OIL Stocks End of June		
	1941	1945	1946	1941	1945	1946	1941	1945	1946	1941	1945	1946
East Coast	22,698	13,570	23,288	1,304	3,431	5,553	10,868	7,493	11,451	7,761	6,544	8,443
Appalachian	3,292	4,264	3,319	166	319	345	376	447	559	539	339	372
District No. 1	.....	2,927	2,311	.....	260	284	.....	348	424	.....	270	223
District No. 2	.....	1,337	1,008	.....	59	61	.....	99	135	.....	69	149
Indiana, Illinois, Kentucky	17,786	19,955	18,267	1,212	1,860	2,050	3,774	4,257	5,400	3,568	2,361	3,832
Oklahoma, Kansas, Missouri	7,595	9,201	8,196	560	707	968	1,397	1,857	2,205	2,066	1,286	1,304
Texas Inland	2,809	2,528	2,882	231	257	372	279	434	376	1,566	865	692
Texas Gulf	13,508	13,830	14,136	3,768	1,479	2,334	8,742	5,830	6,298	8,171	5,606	4,872
Louisiana Gulf	3,351	3,932	3,814	881	840	1,106	1,539	1,833	1,732	1,294	1,004	1,391
Arkansas and Louisiana Inland	710	2,458	1,802	242	172	223	245	761	383	388	213	170
Rocky Mountain	2,306	2,361	2,092	103	119	173	296	347	513	640	721	770
District No. 3	.....	97	93	.....	18	20	.....	23	44	.....	33	41
District No. 4	.....	2,264	1,999	.....	101	153	.....	324	469	.....	688	729
California	16,057	14,029	14,537	1,142	415	757	10,853	9,181	8,845	55,024	16,667	19,700
Total United States	89,842	86,128	92,333	9,609	9,599	13,881	38,369	32,440	37,762	81,017	35,606	41,546

THE MONTH IN THE INDUSTRY

WITHIN a few hours after signing of the dehorned price-control bill which left it free for such action, the oil industry on July 25 inaugurated a wave of price increases. Starting with action by Humble Oil & Refining Company boosting Texas and New Mexico crude oil 25 cents per barrel, the price increases extended throughout the country to become practically unanimous when Standard Oil Company of California on August 1 made increases of 10 to 30 cents per barrel on California crude oil. No increases were announced for areas where stripper payments predominate, for the reason that subsidy payments, while to be continued, are indefinite in that it has not made clear whether the government's premium will be added to the posted price or lowered as the price is increased.

Prices on refined products from refinery to consumer are being increased. Gasoline generally has been increased 1 cent per gallon at filling stations, and fuel oils have increased 15 to 30 cents per barrel. Refinery prices are fluctuating upward in the nearest to a free market that has existed since 1941. The general price increases, incidently, approximate what was in prospect when OPA took charge at the beginning of the war, and also approximate what the industry long has sought from price-control authorities.

While these price adjustments were being made, runs of crude oil to stills during the week ending July 27 were at the high point of the year, and crude-oil production declined slightiy. Refinery runs of 4,896,000 barrels were 116,000 barrels below the peak of the war period a year ago. Gasoline production of 14,535,000 barrels during the week was 700,000 barrels below consumption. However, stocks of all commodities are slightly higher than a year ago.

Conventions

August

25-28—American Institute of Chemical Engineers, Western Section, San Francisco.

September

9-11—Appalachian Gas Measurement Short Course, West Virginia University, Morgantown, West Virginia.

9-13—American Chemical Society, Chicago.

16-20—National Instrumentation Conference and Exhibit, Wm. Penn Hotel, Pittsburgh.

18-20—National Petroleum Association, Hotel Traymore, Atlantic City.

October

3-5—American Institute of Mining and Metallurgical Engineers, Petroleum Division, Galveston, Texas.

11—California Natural Gasoline Association, Annual Fall Meeting, Ambassador Hotel, Los Angeles.

7-12—American Gas Association, Atlantic City.

November

7-8—Society of Automotive Engineers, Fuels and Lubricants Meeting, Tulsa.

11-14—American Petroleum Institute, annual meeting, Stevens Hotel, Chicago.

The price-control-extension bill carries a provision that petroleum and products are to be free of price control until August 20. Thereafter, petroleum and products may be returned to regulation only in the event that a decontrol board set up under the bill finds that the price of crude or any product has risen unreasonably above the maximum price in effect June 30, plus the amount of any subsidy payable thereon, and that the commodity is in short supply and that the public interest will be served by regulation.

The three-pronged formula for recontrol is a club over the head of the industry, to be brought down forcibly if petroleum prices soar, which industry leaders have maintained will not be the case.

Industry, spokesmen, however, were shaking their heads over the manner in which the revived OPA proposes to apply the formula. They point out that no yardstick is provided for what may be considered "unreasonable" prices.

The conference committee accepted the Senate provision for continuation of the stripper-well subsidy until April 1, at not to exceed the existing rates.

Pertinent Sections

Pertinent sections of the bill relating to petroleum are as follows:

(d)(4) Nothing contained in this Act shall be construed to authorize the Administrator to impose or maintain price controls with respect to petroleum or petroleum products processed or manufactured in whole or substantial part from petroleum, except that, after August 20, 1946, maximum prices with respect thereto may be re-established pursuant to the provisions of paragraph (30) of this subsection (d), but only under the standards prescribed in paragraph (8)(c) of subsection (e).

(3) Whenever, after a reasonable test period, it appears that the supply of a non-agricultural commodity which has been decontrolled is no longer consistent with the applicable decontrol standard, the Administrator, with the advance consent in writing of the Price Decontrol Board, shall reestablish such maximum prices for the commodity, consistent with applicable provisions of law, as in his judgment may be necessary to effectuate the purpose of this reflecting their average 1940 price for each product, plus increases in cost since, and to fix wholesale and retail prices at levels which would give distributors their cost of acquisition plus such average percentage discount or mark-up as was in effect March 31, 1946.

All price controls will terminate June 30, next, except as might be specified by Congress in acting on a report to be submitted by the President not later than April 1, 1947, as to what, if any, commodities or classes of commodities are then in such critically short supply as to necessitate the continuance of price controls after June 30. In the meantime, price controls are to be terminated on commodities promptly whenever the supply exceeds or is in approximate balance with demand. Where OPA fails to act promptly, application for decontrol may be filed by industry advisory committees and, if rejected, may be appealed to the price decontrol board.

Recontrol Criteria

The criteria for recontrol of petroleum, as laid down in (8) (C):

(i) That the price of such commodity has risen unreasonably above a price equal to the lawful maximum price in effect on June 30, 1946, plus the amount per unit of any subsidy payable with respect thereto as of June 29, 1946; and

(ii) That such commodity is in short

Trends of Operations and Changes in Stocks

Figures on crude stocks are from Bureau of Mines weekly reports; all others from American Petroleum Institute weekly reports, which are estimates on Bureau of Mines basis.

(All figures in thousands of barrels—add 000)

Trends in Week Ended:	Crude Oil			Gasoline		Gasoil and Distillate		Residual Fuel	
	Production Daily	Runs to Stills Daily	Stocks Week End	Production Weekly	Stocks Week End	Production Weekly	Stocks Week End	Production Weekly	Stocks Week End
1945:									
January 27	4,727	4,756	221,310	14,957	88,223	4,843	33,561	9,252	51,119
February 24	4,777	4,803	219,351	15,500	95,972	4,958	28,753	0,084	46,713
March 31	4,781	4,677	223,782	14,644	98,758	4,548	26,889	9,184	41,745
April 28	4,805	4,780	223,474	14,633	94,068	4,636	28,273	9,379	39,813
May 26	4,887	4,950	222,831	15,194	89,121	4,667	29,184	9,670	38,548
June 30	4,903	4,999	220,781	15,546	86,472	4,910	32,213	9,077	40,488
July 28	4,930	4,996	218,507	16,106	86,008	4,598	36,071	9,586	42,283
August 25	4,892	4,931	211,813	15,986	84,693	4,960	39,782	9,356	46,201
September 29	4,357	3,812	222,387	11,913	79,552	3,940	43,689	7,047	46,853
October 27	4,273	4,838	224,230	15,530	74,335	5,159	43,472	8,691	45,943
November 24	4,469	4,648	219,363	15,681	83,184	4,802	45,258	8,800	47,474
December 29	4,474	4,729	218,918	14,546	95,205	5,055	36,651	8,765	42,447
1946:									
January 26	4,626	4,553	220,544	13,622	107,737	5,720	29,498	8,411	39,722
March 2	4,726	4,779	229,430	13,871	104,462	5,888	25,148	8,634	38,441
March 30	4,425	4,684	221,214	13,896	104,715	5,357	28,240	8,738	37,746
April 27	4,672	4,685	221,689	14,228	99,631	5,568	30,466	9,204	39,404
May 25	4,759	4,857	222,214	14,322	95,769	5,463	32,973	8,908	43,368
June 29	4,957	4,854	223,883	14,500	92,333	5,408	37,762	8,828	46,447
July 27	4,926	4,896	222,740	14,535	88,626	5,817	44,316	8,217	49,517

supply and that its regulation is practicable and enforceable; and

(iii) That the public interest will be served by such regulation.

Stripper Subsidy Problem

Extension of price control, with the provision that the stripper-well subsidy shall continue until next April 1, will raise a problem as to the rate of subsidy to be paid if and as crude prices rise.

Reconstruction Finance Corporation officials who actually disburse the money are understood to be in favor of a reduction in the rate of subsidy as crude prices advance, but OPA officials believe that posted prices should be ignored and the present rates continued without change.

OPA's position is based upon the fact that increased prices for crude based upon advances in cost of labor the fact that increased prices for crude cost of labor and materials will not narrow the spread between flush and stripper-well production, and the latter will be under the same high-expense burden that made adoption of subsidies necessary in the first place.

Since approximately 75 percent of the operating wells use artificial lift, it is felt essential that stripper-well production be protected, and OPA officials do not believe this possible if the subsidies are reduced.

The whole matter is due to be threshed out in the near future, and a directive then will be issued to RFC as to the line it is to follow.

Wants Congress to Give Ample Study to Rubber Program Before Selling Plants

The Senate passed a resolution sponsored by Senator Joseph C. O'Mahoney of Wyoming, prohibiting WAA from immediately disposing of 15 copolymer and 10 petroleum butadiene and 4 alcohol butadiene plants which it reported to Congress June 18 it was planning to sell or lease to private interests.

Under the resolution, disposition of the plants would be deferred until six months after a national rubber program has been submitted to Congress. WAA, however, would be permitted to dispose of styrene, furfural and carbon-black plants and two of the alcohol butadiene plants, and copolymer plants to the extent that their aggregate total rated capacity does not exceed 20 percent of the overall rated capacity of all government-owned copolymer plants.

Calling the resolution up for consideration, O'Mahoney explained that under the law only a 30-day notice to Congress is necessary when it is proposed to dispose of plants costing more than $5 million in the synthetic-rubber and certain other categories.

"It is impossible for the Congress to give it the study it ough to have," O'Mahoney said. "We ought to be sure that our synthetic-rubber industry is not hastily disposed of because we may again be dependent upon foreign sources."

A report by the Senate Military Affairs Committee, approving the legislation, pointed out that the inter-agency policy committee on rubber had not been submitted a report and recommendations with respect to a national rubber program.

Policy Committee Reports

Later the Federal Inter-Agency Policy Committee on rubber declared itself in favor of government subsidies and compulsory use of synthetics as the best way to preserve a synthetic rubber industry for national emergency. The committee noted, however, that such legislation now would be premature because the synthetic rubber industry may prove itself capable of survival without artificial support.

"It is quite possible that cost and quality improvements may be such as to enable synthetic rubber to compete in a free market with natural rubber after the latter is again in amply supply," the committee informed Congress and President Truman in its final report.

The body was appointed last year, under chairmanship of William L. Batt, to draw up plans which would insure that the rubber-tired American economy would not be dependent primarily upon foreign sources for natural rubber, as it was before the Japanese attack at Pearl Harbor in 1941.

Certain recommendations were offered. Endorsed by John R. Steelman, reconversion director, as "highly desirable in the public interest," the major ones were:

That research be stimulated; and to promote private competition in research, that existing agreements to swap inforfation and to cross-license patents among companies be ended as soon as practicable.

That the government put its $75,000,000 worth of plants on the market as soon as it appears that private operators will bid for enough of them to create the core of a "strong diversified private industry"—probably by the year end.

That Congress "declare as essential to the national security of the United States, the maintenance of a synthetic rubber industry whose production will be continuously used."

That Congress create a permament rubber national rubber supervisory body to stand watch over the federal support of the industry, the progress of research, the keeping of stockpiles and the recommending of further legislation to carry out the national rubber policy.

Senate Committee Comment

It originally was planned not to submit a final disposal program for the copolymer and butadiene plants until a national rubber program had been developed, but the recommendation by the Senate Committee for disposal was sent to Congress in June because WAA feared that failure to do so at this time would preclude disposition of the plants until after Congress reconvenes next year. However, the committee commented, WAA reported that the cut-off date for bids on the plants would not be earlier than the end of 1946, indicating that there is no immediate urgency to proceed with the disposal of the basic synthetic rubber plants. At the same time, it was held, interruptions of operations could not be avoided in case of operators, and it seems desirable to postpone disposals until a time when a change over can be effected without damage to the national economy and national security.

The Senate Committee also pointed out that some of the agreements between the government and the present operators of rubber plants contain restrictive provisions with respect to disposal of the plants which are contrary to the objectives set forth in the surplus property act and, further, the present patent picture is "rather complex" and will make it difficult for companies other than the present operators to bid on some plants. Accordingly, time should be given for the study of these situations with a view to negotiating agreements with the present operators which will permit other companies who desire to acquire the plants to operate them in fair competition with the present operators, it was said.

"The fact that Congress desires further study the disposal of the basic synthetic rubber plants should not be any means be constructed as an indication that Congress is opposed to transfer to private ownership of the synthetic rubber industry" the Senate committee emphasized. "On the contrary, the Congress desires to encourage the establishment at the earliest possible date compatible with the national security of a privately owned competitive synthetic rubber industry.

"In view of the importance of the synthetic rubber industry for the national economy in times of peace and for the national defense in times of war, Congress would not fulfill its obligations to the people if it permitted the disposal of synthetic rubber plants without a thorough study of the proposed disposal program within the frame work of an over-all national rubber program."

UOP Formally Opens Physics Research Division

Universal Oil Products Company formally opened its new physics laboratory August 1, a part of the Riverside laboratory in suburban Chicago. The new building houses the enlarged physics research division, which was set up in 1939 when catalysis became a factor in petroleum processing.

Additional equipment and a growing staff made it necessary to provide the larger facilities. The research and development department of Universal Oil Products Company is concerned with all phases of petroleum processing and its laboratories and pilot plants are located on a tract of 27 acres.

Editors, staff writers and business representatives of the oil-trade publications as well as daily publications were guests of the company for the day of the opening. In the morning they gathered at downtown headquarters, 310 South Michigan, where activities of the company were explained by executives. Then the several departments were inspected prior to an inspection of a small-scale model of the new MS-type fluid cracking plant.

After a trip to the Riverside plant, the activities of the research department were explained with especial emphasis on the physics division. Dr. C. H. Ehrhartd outlined the scope of this divi-

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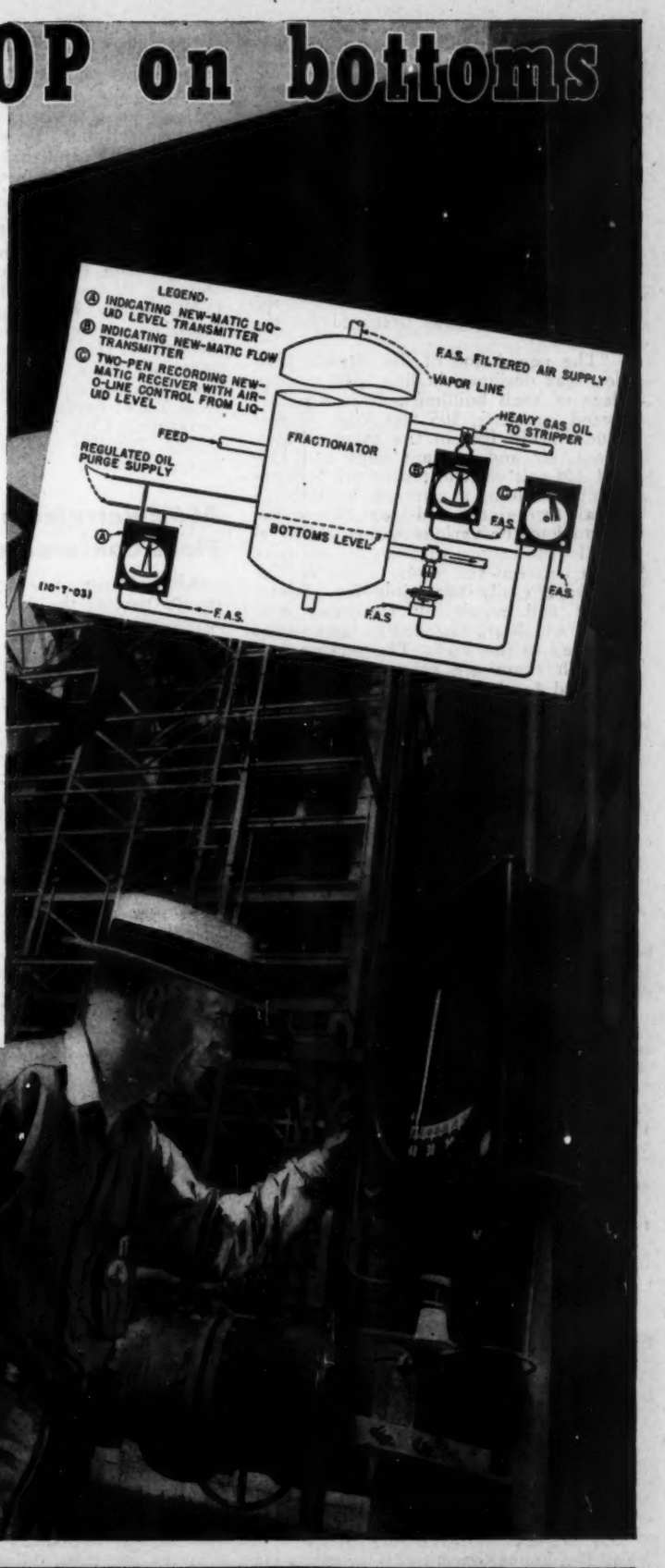

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sion. Then the visitors were privileged to get detailed descriptions of each instrument in the new laboratory. The equipment included: ultraviolet spectrophotometry, infrared spectroscopy; Raman spectroscopy; mass spectrometry; X-ray diffraction, and electron microscopy.

The following description of the building is taken from an explanation of the physics laboratory as prepared for the press:

"The new home of the physics division was designed in line with modern ideas of such buildings. It is a gable-roofed structure, 105 feet long, 32 feet wide and 13 feet to the eaves. Water, steam, air and vacuum lines and 110- and 220-volt electric power are brought into the building in a trench, led through a wall to the attic and from thence distributed to the various rooms by carrying the lines down through the partition walls between the studs. These service lines are easily accessible for maintenance and repair by removing steel plates which are fastened to light angles attached to the studs. The service lines in each room are supported on racks fastened to the wall and are concealed by benches and tables, all of which can be removed when necessary to permit work on the service lines.

"Individual power panels are provided for each room where necessary. The panels are installed in hall partition walls and are of the flash type with the doors opening into the hall. The main power panel is located in the large room used as a general laboratory. With this arrangement, if the power should fail in one room, the others are unaffected.

"The air in the physics building is filtered, warmed (or cooled) and humidified by heating and air-conditioning equipment in the attic. In order to avoid vibration in the building the equipment is supported on pipe columns which are located in the dead space in the partition walls, free from contact with the walls. These columns are set on concrete spread footings and are insulated from the floor by cork expansion joints. Air conditioning and anti-vibration measures are necessary to assure accuracy in the operation of the extremely sensitive apparatus."

After the detailed inspection of the physics laboratory the guests were conducted through other departments of the Riverside plant.

Committee Named to Make API Nominations

A new method of nomination for the American Petroleum Institute, authorized by its board of directors at the recent Dallas meeting, was announced by President William R. Boyd, Jr., with appointment of a committee on nomination.

Heretofore, a nominating committee has been appointed from the floor at the opening session of the board of directors at the annual meeting. The new committee on nomination is charged to meet before the annual meeting, to which it will report, and agree on nominees for officers, members of the executive committee and members of the committee on membership.

Members of the institute are permitted by the by-laws to make suggestions for nominations to the new committee.

Annual meeting of the Institute will be held this year at Chicago, November 11-15.

Members of the committee on nominations are: Robert E. Wilson, Standard Oil Company (Indiana), Chicago, chairman; Robert H. Colley, The Atlantic Refining Company, Philadelphia; H. D. Collier, Standard Oil Company of California, San Francisco; J. C. Donnell, II, Ohio Oil Company, Findlay, Ohio; W. H. Ferguson, Continental Oil Company, Denver; Walter S. Hallanan, Plymouth Oil Company, Pittsburgh; B. A. Hardey, Louisiana Mineral Board, Shreveport; George A. Hill, Jr., Houston Oil Company of Texas, Houston; B. Brewster Jennings, Socony-Vacuum Oil Company, New York; Reese H. Taylor, Union Oil Company, Los Angeles, and H. C. Weiss, Humble Oil & Refining Company, Houston.

ASME Petroleum Committee Plans Conference in Tulsa

After a lapse of several years, activity on the part of the American Society of Mechanical Engineers in the field of petroleum mechanical engineering is promised again through announcement that a three-day conference on petroleum mechanical engineering will be held at the Mayo Hotel, Tulsa, October 7, 8 and 9. Technical sessions will offer nearly 50 papers on production, transportation, refining, products application, and construction materials. One important feature is a contemplated symposium on the design of vessels for high-pressure, high-temperature service.

Approximately 20 sessions will be required to take care of technical papers on the program, these sessions taking place on the afternoon of the first day, and during both mornings and afternoons of the second and third days. It has been possible in arranging the schedule to avoid conflicts of interest to a large extent.

Final programs and forms to facilitate preregistration will be available during the latter part of August, either from the headquarters of the society, at 29 West 39th Street, New York 18, or from the secretary of the Petroleum Committee, E. W. Jacobson, Gulf Research & Development Company, Box 2038, Pittsburgh 30. The committee has urged those who are considering attending to register with the secretary. Hotel reservations are being handled by D. A. Cant, 1312 East 15th Street, Tulsa 4.

Papers have been arranged in five groups. The production program includes 9 papers, the transportation program 9, and the equipment and refining program, 8 or more. The program on construction materials includes 7 papers, and that on applications of petroleum products, three symposiums totalling 9 or 10 papers.

Equipment and refining papers will include discussions on relief valves; control instruments; pressure vessel design; mechanical difficulties in cracking; serrations for tube rolling; hydraulic decoking; compressor developments, and suspended refractory walls. The section on construction materials will include papers on control of acid sludge corrosion; refinery corrosion problems; condenser-tube corrosion; use and properties of certain construction materials including nickel steels for low temperatures, free cutting steels, and cast irons.

Refined Products Imports For U. S. Show Big Gain

Petroleum imports into the United States during May increased by nearly 2,300,000 barrels over April, all of it in refined products, Department of Commerce statistics disclose.

Total imports were 12,450,000 barrels against 10,165,000 barrels in April, consisting of 7,784,000 barrels of crude against 7,867,000 barrels and 4,666,000 barrels of refined products against 2,298,000 barrels.

Product receipts were mostly residual fuel oil, 3,786,000 barrels against 1,833,000 barrels, with 673,000 barrels of distillate fuel oil against 251,000 barrels, 40,000 barrels of asphalt against 109,000 barrels and 167,000 barrels of unfinished oils against 55,000 barrels.

More than half of the total imports came from Venezuela, which furnished 6,608,000 barrels against 6,714,000 barrels in April; Netherland West Indies sent in 4,178,000 barrels against 2,024,000 barrels; Colombia, 886,000 barrels against 926,000 barrels, and Mexico 778,000 barrels against 501,000 barrels.

Bids for Big-Inch Lines Are Highly Involved

Sixteen bids for purchase or lease of the Big-Inch pipe line systems were opened by War Assets Administration July 31.

Five bidders committed themselves to use of the lines for oil transport. The remaining bids contemplated use of one or both lines for gas, either immediately or as an eventuality if oil service proved unprofitable, but it was indicated by WAA officials that a further authorization from Congress would be sought before closing any agreement looking to use of the lines as gas carriers.

J. Watson Snyder, antitrust attorney of the Department of Justice, was present at the opening of bids. The department will have to pass upon any transfer of the lines to private ownership or operation, from the standpoint of the antitrust laws, but there was nothing in any of the bids which appeared would bring them afoul of the department.

The several bids involving the use of the lines for gas were contingent upon issuance of the necessary certificate by the Federal Power Commission, and they also carried provisions for retention in stand-by condition of the oil facilities not required in gas transport to insure quick return of the systems to petroleum service in the event of emergency.

WAA officials said it would require several weeks to complete an analysis of the bids. If one of the proposals involving retention of the lines in oil service is acceptable, it is probable a deal could be worked out without delay, but if it is deemed that the interests of the government will be better served by one of the offers involving conversion to gas, it is expected the matter will have to go over until Congress meets again.

French Refinery Plants Being Rapidly Rebuilt

American oil industry is proceeding satisfactorily with its reconstruction work in Western Europe. Standard Oil Company (New Jersey) has progressed far with reconditioning of its Port Jerome plant on the Seine near Rouen, France. Few trade curbs were invoked despite the fact that the company had

THE MONTH . . .

to purchase most of its materials in the United States.

The Port Jerome refinery, with a daily average capacity of 25,300 barrels before the war, now is handling 12,000 barrels daily. The owner plans not only complete rehabilitation of this property, but elaborate expansion as well. Catalytic cracking equipment and thorough-going modernization are projected for 1950 completion.

Socony-Vacuum Oil Company is not so far advanced with rehabilitation of its Gravenchen plant, located next to the Port Jerome plant. Work is under way on this unit and on the company's refinery at Frontignan, each of which had about 4000 barrels a day capacity.

Many industry officials expect that France will become the refining center of all Western Europe, and the French government is moving along its prewar course of compelling processing operations within its own borders.

Britain is expected to sponsor the same type of program, and already Standard Oil Company (New Jersey) has plans under way for constructing a refinery in England.

WAA Offers to Sell or Lease North Carolina-Virginia Line

The 179-mile Plantation pipe line extention built by the government between Greensboro, N. C., and Richmond, Va., at a cost of $3,405,283, is being offered for sale or lease by War Assets Administration.

With the eight-inch pipe line will go easements for the 30-foot right-of-way, four main-line pumping stations, four delivery terminals, and other facilities.

Atomic Energy As Fuel For Planes Explored

An extensive program of research into the possibilities of operating aircraft on atomic energy will be undertaken by the Fairchild Engine and Airplane Corporation, which has been awarded a contract by the War Department, in collaboration with other aircraft engine companies, the Manhattan Engineering District and the Army Air Forces.

The work of ascertaining whether atomic energy can be substituted for gasoline or rocket fuel as a propellant for airplanes is purely exploratory, it was indicated by Major General Curtis E. LeMay, Deputy Chief of Air Staff for Research and Development, who is directing the project.

LeMay said security requirements precluded disclosure of details of the plan, but no final solution has been found and no date for completion of the project can be predicted.

Inter-Agency Oil Group Holds Organization Meet

Members of the interdepartmental oil committee, which will be a counterbalance to the National Petroleum Council in an advisory capacity to the Interior Department's Oil and Gas Division held their initial meeting with Acting Director Ralph K. Davies and other division officials July 19.

The meeting was merely organizational and exploratory, and will be followed by a survey of all government petroleum and gas activities to see how responsibilities are divided, etc.

It was explained that the interdepartmental committee will not seek new ways in which to inject government control into the oil situation.

Members of the interdepartmenal committee are Charles B. Rayner, petroleum adviser to the State Department; Colonel Gustav Vogel, executive officer of the Army-Navy petroleum board, representing the War Department; Captain B. B. Biggs, deputy executive officer of the Army-Navy petroleum board, representing the Navy Department; Nelson Lee Smith, vice chairman of the Federal Power Commission and in charge of the natural gas investigation; Barry Magdoff, special assistant to the Secretary of Commerce and Raymond E. Kerr, director of transportation and fuels branch, Civilian Production Administration.

Asphalt Plant

United Asphalt Corporation, a new company will build an asphalt plant at Heidelberg, Mississippi, near the Heidelberg oil field. The plant which will have a daily capacity of 2000 barrels will be built as soon as a charter is obtained.

Two Gary, Indiana, men head the company, Lawrence G. Bennett as president and C. M. Page, executive vice president. B. C. Burns of Heidelberg is secretary-treasurer.

Stanolind Has Gas-Saving Program Underway in Texas

Stanolind Oil & Gas Company is engaged in an extensive development of its gas resources in Texas with the object of eliminating flare gas. In West Texas, the company has been selected as operator of a gasoline plant in the Slaughter area to be built jointly with Honolulu Oil Corporation, Magnolia Petroleum Company and The Texas Company. Stanolind also contemplates plants in North Cowden, South-Cowden-Foster-Johnson and Fullerton areas. In East Texas, development is underway on a plant in the Carthage area. In the Lower Gulf Coast area, the company proposes to unitize the Burnell-North Pettus areas and construct a cycling plant. A plant already is under construction in the Hastings field, near Houston. Altogether, the company's plans calls for utilization of 130,000,000 cubic feet of gas daily.

CNGA Directors Install Officers, Committees

The annual meeting of the board of directors of California Natural Gasoline Association at the Biltmore Hotel in Los Angeles on July 9, was the occasion for announcement of officers, directors and committees for the fiscal year 1946-47. M. W. Kibre of General Petroleum Corporation, replaced M. L. Arnold as president; F. J. Colton, Tide Water Associated Oil Company, Los Nietos, is vice president, and George L. Tyler is secretary-treasurer. Four new members were elected to the board of directors: Coles B. Bason, Ingersoll-Rand Company; H. L. Eggleston, General Petroleum Corporation; C. L. Hutchings, Tide Water Associated Oil Company, and R. C. Patterson, Belridge Oil Company. George F. Howells, Tide Water Associated Oil Company, and chairman of the Taft chapter of the association, also is a new director. Tyler's reappointment is for the ninth year.

In reviewing the affairs of the association for the past fiscal year, it was pointed out that membership has increased steadily, and the work of the technical committees which continued throughout the war period has resulted in a number of revisions and new bulletins soon to be released. A noteworthy accomplishment of the past year was the enlarging and improvement of the association's monthly report of natural-

New Officers and Committee Chairmen, California Natural Gasoline Association

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President

F. J. COLTON
Vice President

E. A. BROCK
Membership Committee

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Program Committee

E. G. RAGATZ
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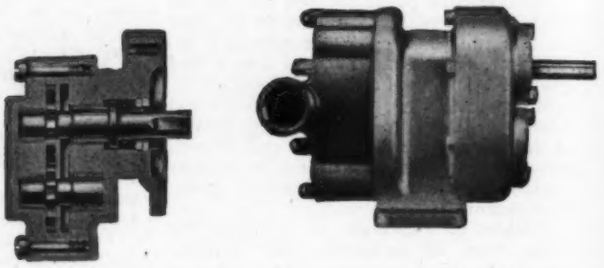

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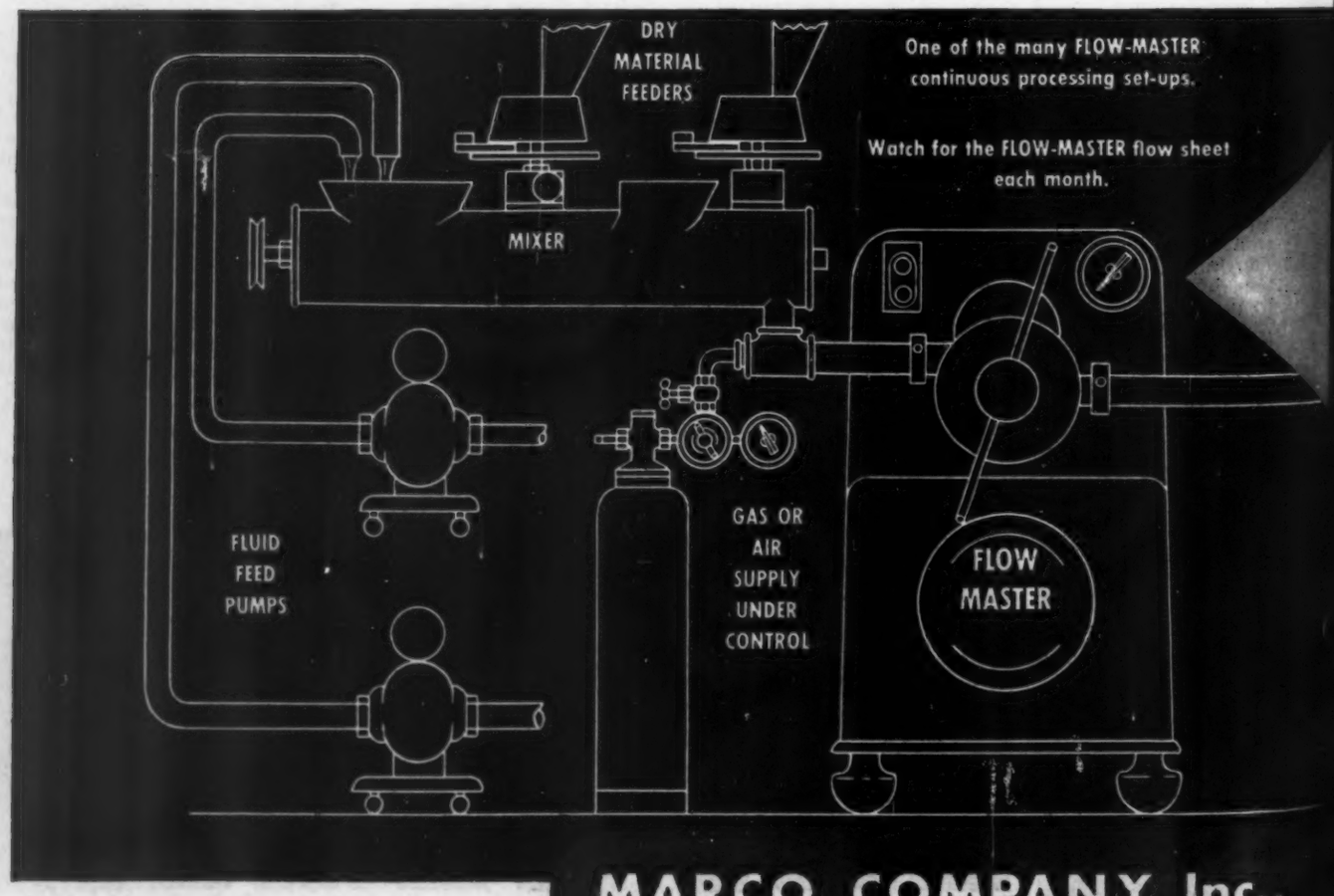

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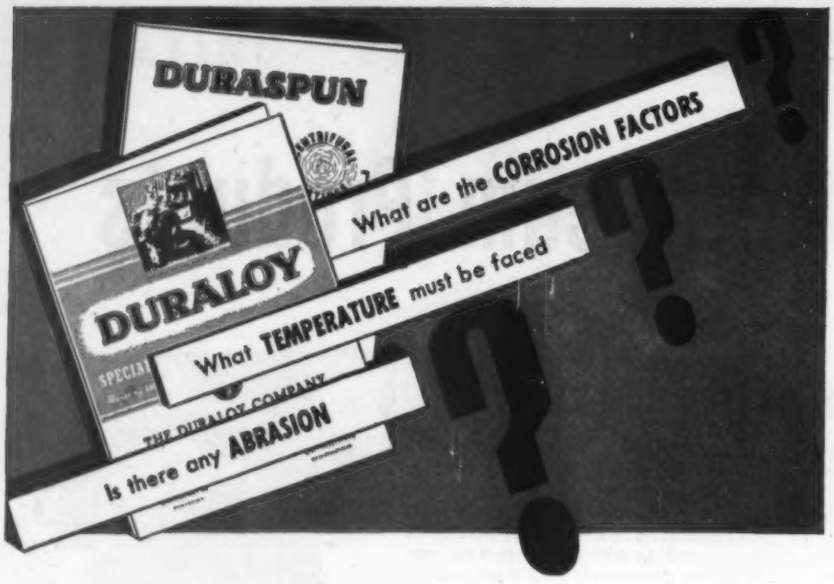

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gasoline and cycling-plant operations, natural-gasoline and LPG production data, and natural-gas production and disposition information.

The association continues to cooperate actively with other technical groups and recently has received confirmation of E. P. Valby, technical committee chairman, as the CNGA representative on the ASTM Technical Committee H on Light Hydrocarbons.

The annual fall meeting of the association is scheduled for October 11 at the Ambassador Hotel, Los Angeles. General chairman of the event is E. G. Ragatz, Bectel Bros.-McCone Company.

Shea Named Vice President Carter Oil Company

Paul C. Shea, who has been acting manager of manufacturing for The Carter Oil Company, has been elected a vice president and member of the board of directors of the company. He will move headquarters from Billings, Montana, to Tulsa, and will direct all refining activities of the company. Robert B. Corran, division manager for the company at Billings and a director, also was elected a vice president.

Shea was a vice president of Colonial Beacon Oil Company and in charge of Manufacturing for that company at Everett, Massachusetts, when he was given leave of absence in August, 1945, to go to Billings as acting manager of manufacturing for The Carter Oil Company. He is a graduate of Northeastern University, Boston, and had been associated with Colonial Beacon Oil Company since 1926.

Texas A&I Planning Gas Short Course in August

Improvements in transmission facilities and industrial utilization will be stressed at the Texas College of Arts and Industries short courses in gas technology at Kingsville August 27-29.

Sponsored by the Southern Gas Association, the course will include 12 hours in classroom and laboratory instruction, two general assemblies, and field trips to gas fields and cycling plants in the vicinity of the college. In addition, there will be demonstrations of late-type equipment owned by the college.

Dr. Frank H. Dotterweich, head of the A. & I. engineering department, is chairman of the administrative committee. Robert R. Sutyle, managing director of SGA is cooperating.

Texas A&M Plans Instrument Short Course in September

Agricultural and Mechanical College of Texas will offer its first short course on Instrumentation for the Process Industries at College Station on September 4, 5 and 6. The program will cover a wide variety of subjects of value especially to instrument, process design and operating engineers. Problems of instrument maintenance will not be covered specifically in the lectures but opportunity for consideration of such problems will be provided in discussion

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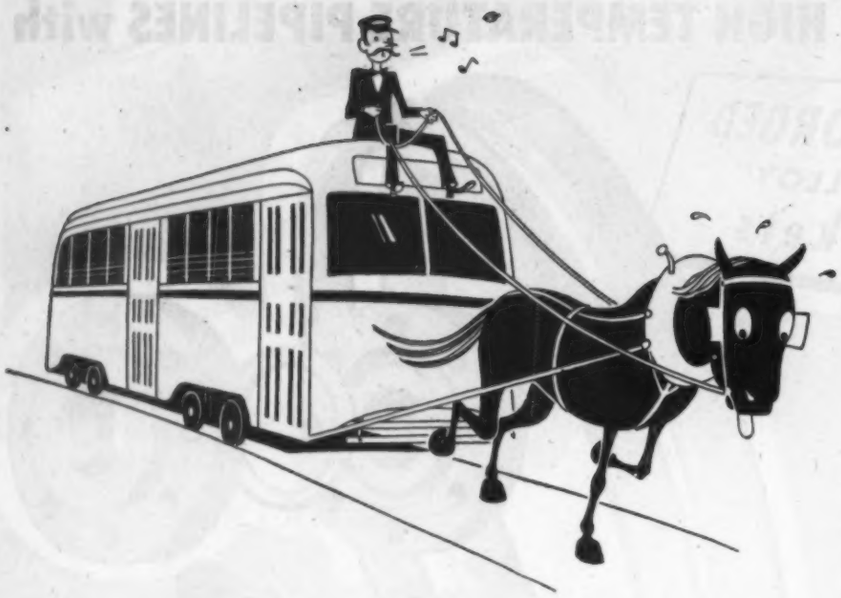

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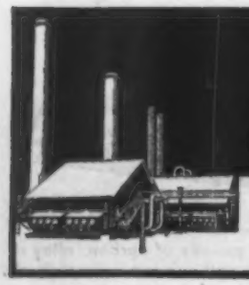

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THE MONTH...

periods. Lectures will cover measurement and control of temperature, pressure and liquid level, time control, and allied subjects. Relationship between practice and basic control theory will be stressed.

Cooperating with the college in presenting the course will be a number of manufacturers of oil, gas and chemical products. Manufacturers of instruments and controls are to take part by arranging educational exhibits and providing lectures for many of the sessions.

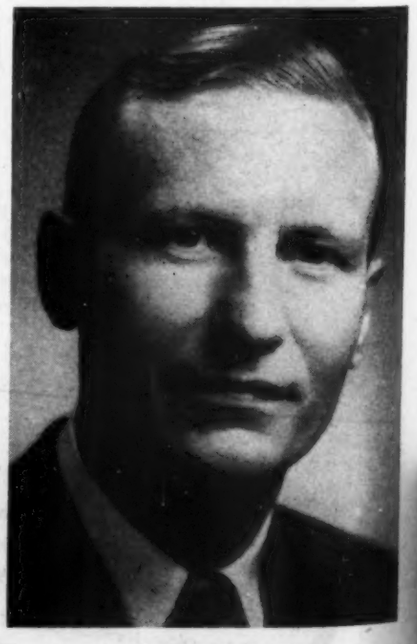
A registration fee of $5 is required for the course which is open to residents outside of as well as within Texas; preregistration by mail is being encouraged. Sleeping accommodations and meals will be available on the campus at reasonable rates. An evening banquet and entertainment also are planned.

Those wishing additional information have been requested to write to Professor P. G. Murdoch, Department of Chemical Engineering, Texas A. & M. College, College Station, Texas.

Miller Heads Standard of California Manufacturing

O. N. Miller has been appointed general manager of the manufacturing department of Standard Oil Company of California, in charge of the Richmond, El Segundo and Bakersville. Only 37 years old, he is the youngest man to hold this key position in the company's history. He succeeds C. E. Finney, Jr., who became a vice president of the company in January.

Miller joined the company in 1934 after receiving his doctor's degree in chemical engineering at the University of Michigan. He first worked in research and development, specializing on cracking problems. Subsequently he became assistant superintendent of the cracking division at El Segundo and then was transferred to the manufactur-



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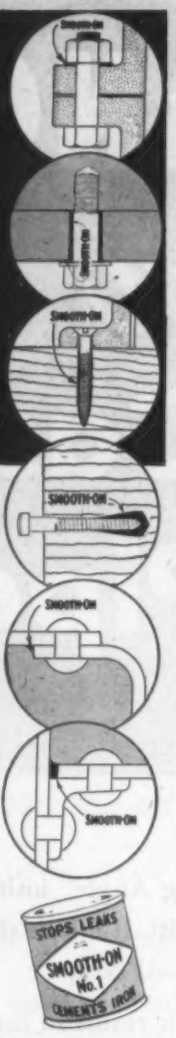

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ing department in the San Francisco office in 1942. The following year he was transferred to Arabian American Oil Company, where his work included planning and designing of the Ras Tanura refinery in Saudi Arabia. On completion of this assignment, he became assistant to the general manager of the manufacturing department and then returned to El Segundo as superintendent of the cracking division. In January he became assistant to the vice president in charge of manufacturing, which position he has held till his present appointment.

Dr. Willard H. Dow Gets Chemical Industry Medal

Dr. Willard H. Dow has been awarded the Chemical Industry Medal for 1946, it is announced by Sidney D. Kirkpatrick of New York, chairman of the American Section of the Society of Chemical Industry.

President and chairman of The Dow Chemical Company of Midland, Michigan, wartime leader in the production of synthetic rubber and pioneer in seawater chemistry, through which science and industry recover raw materials from the ocean, Dr. Dow was cited for his "conspicuous service to applied chemistry."

Dr. Dow also is president of Ethyl-Dow Chemical Company, which extracts bromine from sea water for use as an ingredient of Ethyl fluid. The recovery of bromine off Kure Beach, Wilmington, North Carolina, was the first successful attempt to exploit the mineral riches of the ocean.

Under Dr. Dow's direction, The Dow Chemical Company carried out for the government more than 50 major wartime projects involving magnesium, styrene, high-octane gasoline and basic chemicals required for the manufacture of munitions.

As the only American producer of magnesium at the beginning of World War II, the company not only expanded its own output but designed and operated additional facilities for Defense Plant Corporation. The company also was the only American maker of styrene at the start of the war, and the entire government styrene program was built around the Dow process, with the company operating two government-owned plants and a Canadian factory as well as its own plant at Midland.

Besides supervising the extensive war work at the company, Dr. Dow, who had been a member of the Engineers Reserve Corps and later of the regular Army in World War I, served during World War II on the Chemical Advisory Committee of the Army and Navy Munitions Board, and on the Chemical Warfare Service Advisory Board.

The Chemical Industry Medal, which will be presented at a dinner at the Hotel Commodore in New York on November 8, is the third high scientific award won in recent years by Dr. Dow, who is a director of the American Chemical Society. He received the Chandler Medal conferred by Columbia University for distinguished achievement in science and industry in 1943, and the Gold Medal Award of the American Institute of Chemists in 1944.

Born in Midland on January 4, 1897,

DR. WILLARD H. DOW

he is the son of the late Dr. Herbert H. Dow, who founded the Dow Company that year. Dr. Dow graduated at University of Michigan in 1919 with the degree of Bachelor of Science in Chemical Engineering. He holds the honorary degrees of Doctor of Science, conferred by Michigan College of Mining and Technology in 1939, and Doctor of Engineering, conferred by the University of Michigan in 1941, and by Illinois Institute of Technology in 1944. He began his career with The Dow Chemical Company in 1919 as a chemical engineer, and served in various other positions in the company's several plants for the next few years. He was made a director of the company in 1922 and assistant general manager in 1926. After his father's death in 1930, he took over the duties of president and general manager. He became chairman of the board in 1941.

Dr. Dow is a director of the Midland Ammonia Company, Dowell Incorporated, Dow Magnesium Corporation, Dow Chemicals of Canada, Ltd., and Dow Corning Corporation.

In addition to his industrial and professional interests, he is active in educational affairs as a member of the corporation of Massachusetts Institute of Technology, and of the board of control of Michigan College of Mining and Technology. He is also a member of the American Institute of Chemists, the American Institute of Chemical Engineers, Tau Beta Pi, Alpha Chi Sigma and Theta Delta Chi.

ACS Petroleum Division to Celebrate 25th Anniversary

More than 1000 chemists from the laboratories of the oil industry and the technical schools will celebrate the twenty-fifth anniversary of the organization of the Petroleum Division of the American Chemical Society at Chicago during the week of September 9.

Numerous addresses dealing with problems of the industry will be delivered at sessions to be held in connection with the Society's 110th national meeting, according to an announcement

Reforming Organic Gases at Higher Temperatures, Faster Rates

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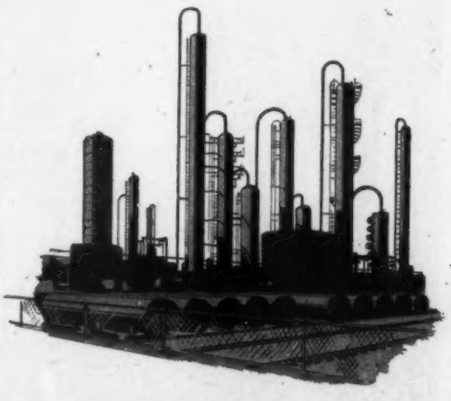

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by Dr. Stewart S. Kurtz, Jr., of Sun Oil Company, chairman of the Division.

Bruce K. Brown of Chicago, general manager of reseach and development of Standard Oil Company (Indiana), will speak on "Petroleum from 1921 to 1971" at a dinner on Tuesday evening, September 10.

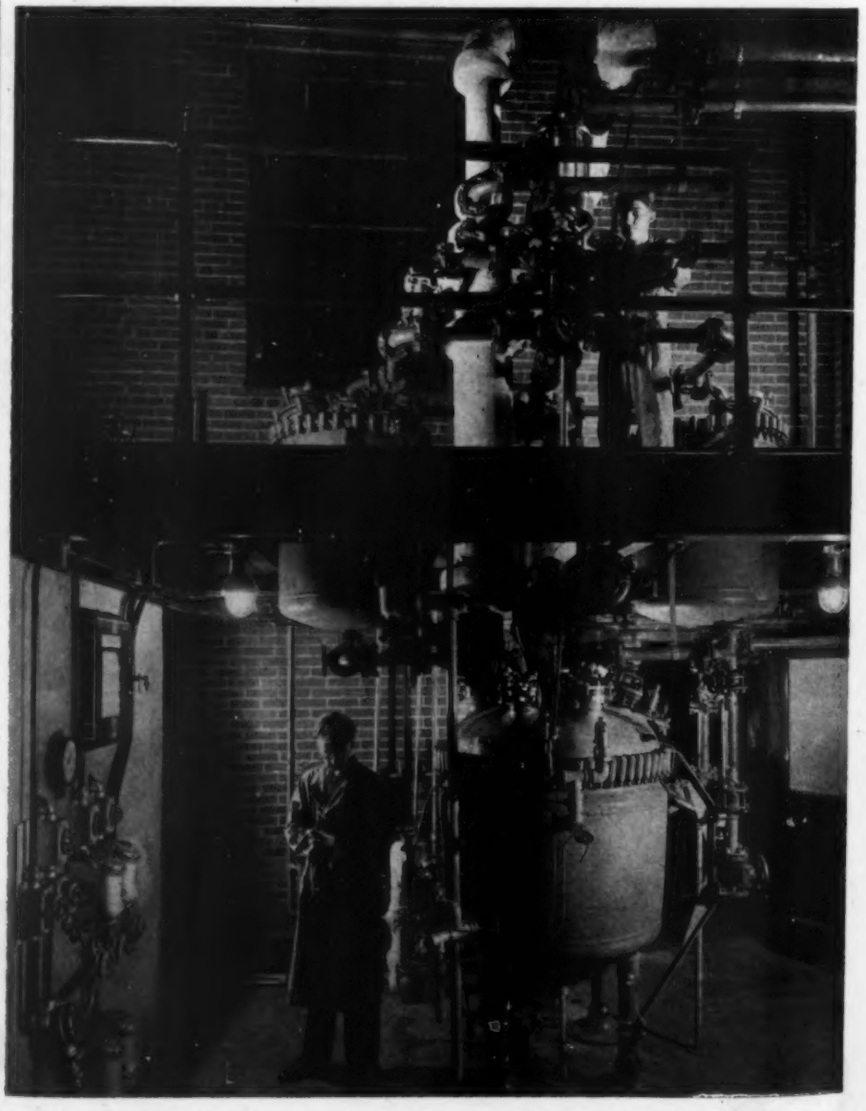
Dr. Charles L. Thomas, research director of Great Lakes Carbon Company, Chicago, is directing arrangements for the celebration. Dr. Thomas is vice-chairman of the division, which with 1300 members is the largest of the society's eighteen professional divisions.

Battelle Institute Installs New Laboratory Facilities

New chemical engineering laboratory facilities for the investigation of industrial processes and products on a pilot-plant scale have been installed at Battelle Institute, Columbus, Ohio.

Among the facilities of the enlarged laboratory is a glass-enameled unit, consisting of a 150-gallon steam-jacketed reaction and distillation kettle, fractionating column, condenser, and two 100-gallon feed or receiver vessels, for operation at moderate pressure or under vacuum. Auxiliary stainless-steel equipment includes a stainless-steel pressure filter and the usual equipment needed for measurement and control in studies of the unit operations involved in industrial processes. By the end of the year, the installation of a 20-inch centrifuge, a 1 x 6-foot rotary warm-air drier, an 8-inch diameter continuous extracting column with additional glass-lined vessels, and a 10-inch diameter solvent or hydrocarbon still is expected to be completed.

Although the recently completed unit was built to provide operating and design data for the production of special organic acids and esters developed in Battelle research, it has been made flexible enough to be used for other purposes. This unit, together with the other facilities of the laboratory and the facilities of the institute's high-pressure laboratory, provides equipment for large-scale studies of several different types of reactions and is available to organizations interested in development work on new processes.



Pilot plant in chemical engineering laboratory of Battelle Institute, Columbus, Ohio.

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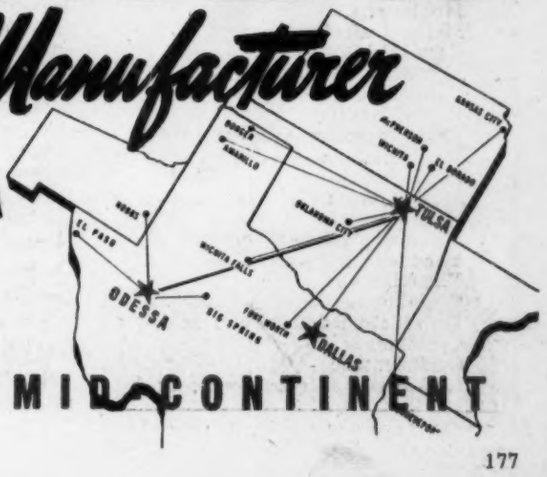

Service That COVERS The MID-CONTINENT

SCIENCE AND TECHNOLOGY ABSTRACTS

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The abstracts here presented are selected from the current literature of science and technology to afford reference to fundamental information not easily available to all readers. Abstracts of articles appearing in readily obtainable trade journals are not included.

Photostat copies of original articles will be supplied at cost by The Leslie Laboratories. Complete or limited bibliographies covering special topics by title, by abstracts, or in complete manuscript, will also be prepared and furnished at reasonable cost by the Laboratories.

Fundamental Physical and Chemical Data

Equation Relating Density, Refractive Index, and Molecular Weight for Paraffins and Naphthenes. M. R. LIPKIN AND C. C. MARTIN, *Ind. & Eng. Chem.*, Anal. Ed. **18** (1946) pp. 380-82.

The authors present an equation relating refractive index for the sodium D line, density, and temperature coefficient of density, each at 20° C, for paraffins, naphthenes, and mixtures of saturated hydrocarbons in the liquid state. The temperature coefficient of density at 20° C. is obtained from molecular weight using the correlation of Lipkin and Kurtz. This equation correlates density and refractive index for all saturated hydrocarbons more accurately than previous equations, but it is not accurate for the calculation of molecular weight. The equation can be applied to hydrocarbon solutions, such as saturated petroleum fractions, for the reason that it does not require a knowledge of molecular formula or structure. Refractive index can be calculated from density and the temperature coefficient of density to an accuracy of ±0.002 for pure hydrocarbons and ±0.001 for petroleum fractions. Also, density can be calculated from refractive index and the temperature coefficient of density to an accuracy of ±0.004 and ±0.002, respectively. The equation gives the basis for further correlations that will serve as tools in the analysis of hydrocarbon solutions. Detailed data are presented in four tables and one figure, and a bibliography of 18 references is included.

Chemicals Wanted

The National Registry of Rare Chemicals, Armour Research Foundation, 33rd, Federal, and Dearborn Sts., Chicago 16, Illinois, has received urgent requests for the chemicals listed below. If anyone has one or more, even if only one gram quantities, please inform the Registry.

Butoxy acetic acid
Montanyl alcohol
Melissyl alcohol
Ceryl alcohol
Myricyl alcohol
Carnaubyl alcohol
Propyl nitrate
Ethyl isopropyl ketone
Propyl nitrite
Hexanone-3
Methyl nitrate
Silicon trichloride
2-Phenyl cyclohexanol
Phenoxazine
Phenyl sulfate
Cyclobutene
Benzene hexacarboxylic acid
Cyclobutane
Cyclopentene
1,2,3-Benzene tricarboxylic acid

An Equation for the Line of Saturation of Liquids and Vapors. J. E. HAGGENMACHER, *Jour. Amer. Chem. Soc.* **68** (1946) pp. 1123-26.

No single mathematical relationship comprising all four variables of saturated fluids has been published. The author derives a simple expression for the relationship between vapor-volume, liquid-volume, pressure and temperature that affords a mathematical expression of the line of saturation. Expressions for the sum and for the difference of the volumes of saturated liquids and vapors are deduced. The relationship was tested on 58 substances and was found to be more accurate than 3-constant equations such as van der Waals' or Berthelot's.

The Thermodynamics of 2,2-Dimethylbutane, Including the Heat Capacity, Heats of Transition, Fusion and Vaporization and the Entropy. J. E. KILPATRICK AND K. S. PITZER, *Jour. Amer. Chem. Soc.* **68** (1946) pp. 1066-72.

The heat capacity of 2,2-dimethylbutane was measured from 15 to 280° K. and the vapor pressure from 211 to 290° K. The values obtained were: heats of transition, 1289.2 ± 3 cal./mole at 126.81° K.; 67.7 + 1 cal./mole at 140.88° K.; heats of fusion 138.5 ± 05 cal./mole at 174.16° K.; entropy at 298.16° K.; 65.13 ± 0.15 for the liquid and 85.72 ± 0.2 cal./degree mole for the ideal gas. A vibrational assignment is made and the average potential barrier to internal rotation was calculated as 4375 cal./mole. The experimental entropy agrees satisfactorily with the value calculated by one of the authors in 1940, which supports the general method then employed. Data are presented in considerable detail in 12 tables and 2 figures.

The Heat Capacity, Vapor Pressure, Heats of Fusion and Vaporization of Cyclopropane. Entropy and Density of the Gas. R. A. RUEHRWEIN AND T. M. POWELL. *Jour. Amer. Chem. Soc.* **68** (1946) pp. 1063-66.

The heat capacity of solid and liquid cyclopropane was measured from 15° K. to the boiling point. The melting and boiling point temperatures were found to be 145.54 and 240.30° K., respectively. The heats of fusion and vaporization were determined by calorimetric observation to be 1301 and 4793 cal. mole^{-1}, respectively. The vapor pressure of liquid cyclopropane was measured and the data were found to be represented by an equation, which equation is given. The density of cyclopropane gas at 298.10° K. and one atmosphere pressure was found to be 1.7463 g./liter. The calorimetric data were used to calculate the entropy of cyclopropane gas and the value so obtained compared with one obtained from molecular data. It was found that the entropy of cyclopropane approaches zero near the absolute zero of temperature. The most reliable value of the entropy is the one obtained from molecular data, 56.84 cal./deg. per mole at 298.1° K. and one atmosphere. This value does not include the nuclear spin entropy

Heats, Equilibrium Constants, and Free Energies of Formation of the Acetylene Hydrocarbons Through the Pentynes, to 1500° K. D. D. WAGMAN, J. E. KILPATRICK, K. S. PITZER, AND F. D. ROSSINI. *Res. Paper RP 1682. J. Res. Nat'l Bur. Stand.* **35** (1945) pp. 467-96.

The thermodynamic properties of seven acetylene hydrocarbons, C_2 to C_8, were investigated. The heat content, free energy, entropy, were calculated for acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, and 3-methyl-1-butyne in the gaseous state at temperatures up to 1500° K. The data so obtained were then combined with values of heats of formation at 25° C. to calculate the values of the heats, free energies and equilibrium constants of these acetylenes, and also values of free energies and equilibruim constants of isomerization of the two butynes and the three pentynes. Values of the free energies and equilibruim constants of dehydrogenation of the C_2 to C_8 paraffin and olefin hydrocarbons were also calculated. Data are presented in some detail in tabular and graphical form.

Thermodynamic Properties of Gaseous 1,3-Butadiene and the Normal Butenes Above 25° C. Equilibria in the System 1,3-Butadiene, n-Butenes, and n-Butane. J. G. ASTON, G. SZASZ, H. W. WOOLLEY, AND F. G. BRICKWEDDE, *J. Chem. Phys.* **14** (1946) pp. 67-79.

Tables of the thermodynamic functions are given for 1,3-butadiene and normal butenes for temperatures from 298.16° K. to 1500° K. for the substances

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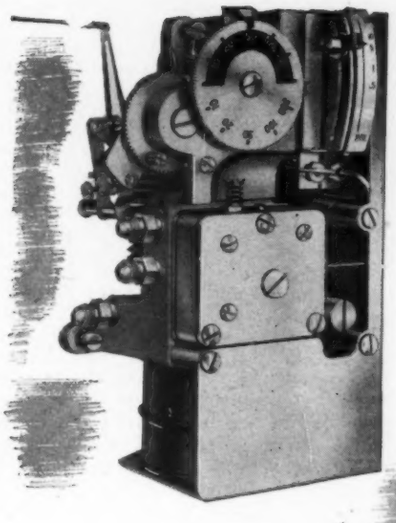

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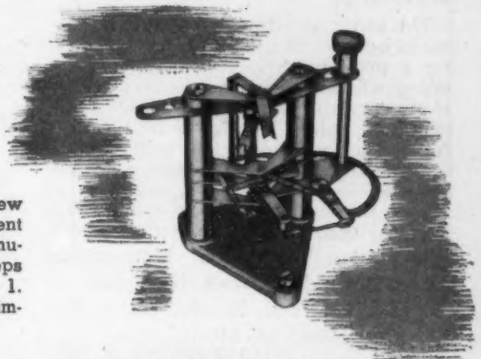

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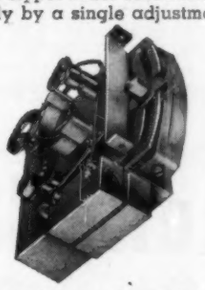

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in the gas states at atmospheric pressure. The tables are based on reliable spectroscopic and molecular data, together with calorimetric entropies, gaseous specific heats, and heats of formation. Equilibrium constants for reactions in the system 1,3-butadiene, n-butenes, and n-butane are given. Such experimental data as are available are compared with the calculated data. The calorimetric data for 1,3-butadiene indicate the existence of two geometric (cis-trans) isomeric forms. These are present in appreciable concentrations at room temperatures. The two forms differ in energy by 2.3 kcal. mole^{-1}, and are separated by a C-C rotational barrier 2.6 kcal. mole^{-1} above the lowest energy level of the cis, or higher energy form.

The Purification and Physical Constants of Aromatic Hydrocarbons. L. C. GIBBONS, ET AL, *Jour. Amer. Chem. Soc.* **68** (1946) pp. 1130-31.

The physical properties of eleven aromatic hydrocarbons were obtained during a program involving the synthesis and purification of ten-gallon quantities of twenty-six aromatic hydrocarbons. Freezing point, boiling point, density, and refractive index are reported for benzene, toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, o-xylene, p-xylene, m-diethylbenzene, p-cymene, 1,3,5-triethylbenzene, and 3,5-diethyltoluene.

Molecular Volumes of Mononuclear Aromatic Hydrocarbons. N. CORBON, M. ALEXANDER, AND G. EGLOFF. *Ind. & Eng. Chem.* **38** (1946) pp. 610-11.

The work reported correlates existing density data and structure for fourteen homologous series of mononuclear aromatic hydrocarbons, and thus provides a method for estimating the molecular volumes and densities of unknown or unmeasured properties of members of these series. The molecular volumes of 1-phenylalkanes and 2-phenylalkanes at any given fraction of the critical temperature are linear functions of the number of carbon atoms. The relationships can be expressed by equations of the form:

$$M/d = V = a + bn$$

Constants a and b are simple functions of the reduced temperature. These functions can be expressed by equations of the form:

$$a \text{ or } b = k + pT_R + qT^2_R$$

Chemical Compositions and Reactions

Polymerization of Olefins and Diolefins in Suspension and Emulsion. I. W. P. HJHENSTEIN AND H. MARK, *J. Polymer Sci.* **1** (1946) pp. 127-45.

The authors review the literature on the mechanism of polymerization of olefins and diolefins in aqueous suspensions and emulsions from 1910 to 1945. New data are also given on the initial rate of polymerization of styrene and other vinyl compounds; on the effect of water-soluble activators, such as sodium sulfite, on the effect of initial size of monomer droplets, on the size of monomer droplets and polymer particles throughout polymerization, and on side reactions at higher concentration. Polymerization in suspension is discussed in detail including procedure, stabilizers, and quantitative relationships. Tables are given showing data on general conditions for forming various bead sizes in the suspension polymerization of different monomers, on suspension poliymerization and copolymerization of olefins and diolefins with ethylene glycol as a suspending medium, on copolymers of olefins and diolefins prepared by suspension polymerization, and on monomer-soluble and water-soluble catalysts.

Oxidation of Lubricating Oils. H. H. ZUIDEMA, *Chem. Rev.* **38** (1946) pp. 197-226.

The author proposes mechanisms for the oxidation of paraffins, naphthenes, and aromatics under conditions comparable to those encountered by lubricating oils in service. Hydroperoxides are believed to be first formed. These decompose to form acids, ketones, aldehydes, and other intermediate oxidation products. These products in turn can oxidize further or can condense. Condensation products are formed predominantly in the oxidation of aromatics. Rate of oxidation depends upon structure. Paraffins and naphthenes oxidize at an intermediate rate. The introduction of unsaturation or a partially hydrogenated aromatic ring into the molecule increases its rate of oxidation. The addition of a benzene ring at the end of a long paraffin molecule increases the rate. The presence of a naphthene nucleus has the effect of stabilizing the molecule. In general, the rate of oxidation of hydrocarbon solutions is not the mean of the rates of the individual components, but is quite different. The component that is most stable when treated alone

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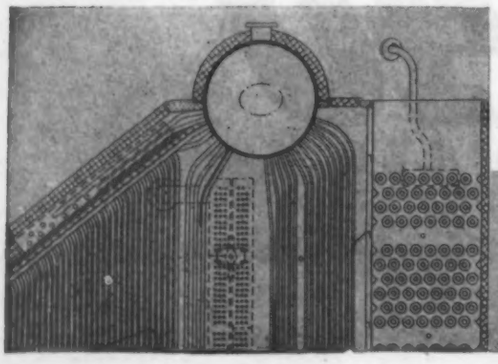

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Photo of Tube Bundle for Type FST Cooler. Courtesy Griscom-Russell Company.

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may be preferentially oxidized in a solution of several components. Compounds of copper, lead, and iron that may be present in small concentration often exert a large accelerating effect upon the overall rate of oxidation. A bibliography of 45 references is included.

Analysis for Naphthene Ring in Mixtures of Paraffins and Naphthenes. M. R. LIPKIN, C. C. MARTIN, AND S. S. KURTZ, JR., *Ind. & Eng. Chem.*, Anal Ed. **18** (1946) pp. 376-80.

The authors recommend a new method based on the temperature coefficient of density and either density or refractive index for the analysis of ring content in mixtures of paraffins and naphthenes. When tested with known solutions the procedures shows an average deviation of 8%, which is occasioned principally by the isomer effect. The accuracy of the method is dependent to some extent on the degree of condensation of the naphthene rings. It is unsatisfactory for bridged ring naphthenes and single naphthene rings containing more than eight carbon atoms in the ring. The new method is compared to several older methods. Data secured in the work are presented in considerable detail in eight tables and four figures, and a bibliography of 24 references is included.

Manufacture: Processes and Plant

Material or Heat Transfer Between a Granular Solid and Flowing Fluid. E. W. THIELE, *Ind. & Eng. Chem.* **38** (1946) pp. 646-50.

The author reviews the work so far reported in the literature on the computation of the transfer of material (or heat) when a fluid (liquid or gas) is passed through a bed of granular solid, as in the decolorization of liquids, the recovery of volatile solvents, heat recovery in furnace regenerators, or removal of material from air by gas masks. It is noticed that there is no generally accepted term for this broad class of operations; the term "percolation" seems convenient and suitable, although not entirely free from objection. The unit operation of percolation has been but little discussed in chemical engineering texts. Nevertheless, for the last twenty-five years, materail for a theory of the operation has been accumulating, and progress has been especially rapid in the last few years. For the transfer of a single material, where equilibruim between fluid and solid can be assumed, the problem has been completely solved. Some progress has been made in handling cases of multiple transfer of materials. For the transfer of a single material where the rate of approach to equilibrium is finite, numerous special cases have been solved. However, for more than one material transferred, little has been done. The need at present is for a better experimental basis for the development of the entire subject. A bibliography of 29 references, including articles of importance to date, is included.

Temperature Efficiency in Distillation. M. NORD, *Ind. & Eng. Chem.* **38** (1946) pp. 657-58.

In the fractional distillation of binary systems in plate columns, the temperature on a plate can be used as a measure of plate efficiency. The author presents an equation for temperature efficiency, and continues with derivations showing the similarity between equations for temperature efficiency and diffusion efficiency.

Synthetic Fuels in Germany. *I. Introduction Petroleum* (London) **9** (1946) pp. 74, 96.

For the manufacture of synthetic fuels the Germans used both the Fischer-Tropsch synthesis and the hydrogenation of coal. In the hydrogenation process the coal is treated to produce stable liquids by the action of hydrogen under pressures of about 200 atmospheres or more. In the Fischer-Tropsch process the coal is first converted to a gaseous mixture of CO and H_2, from which liquids are synthesized catalytically at atmospheric pressure. Products from the hydrogenation process are largely aromatic, while those from the Fischer-Tropsch process are entirely paraffinic or olefinic. Attention was given largely to increasing production to the maximum rather than to developing new processes. A plant was operated in Holland to convert C_{12}-C_{14} olefins to aldehydes by passage over cobalt catalysts at 150 atmospheres pressure and 180° C. The alcohols made were used in the manufacture of sulfonic ester soaps. The D. H. D., or dehydrogenation high pressure process, involved catalytic dehydrogenation of naphthenes to aromatics at 50 atmospheres and 500° C. The yield of aromatized fuel was said to be 65 percent of the feed stock. The isobutane was separated and dehydrogenated to isobutylene. An alkylation plant converted butylene and butane to isooctane.

Process Development and Production of Isohexane and Isoheptane as Aviation Fuel Components. S. F. BIRCH, P. DOCKSEY AND J. H. DOVE, *Jour. Inst. Petr.* **32** (1946) pp. 167-199.

Early in 1940 the main components of 100 octane fuel were either hydrocarbon fractions isolated from crude oil by physical means, such as distillation or solvent extraction, or, alternatively, hydrocarbon fractions produced by synthetic processes, such as cracking, alkylation, and catalytic polymerization followed by hydrogenation. These components were then blended with a suitable base stock and tetraethyllead to give the 100 octane fuel. It was because of difficulty experienced in the production of a suitable base stock that a program of work was started and which culminated in 1944 in the production of 315,000 gallons per day of refined isohexane and isoheptane fractions, which represented about 35 percent of the daily output of 100-octane aviation fuel from the Anglo-Iranian Oil Company Refinery at Abadan. These hydrocarbon components were made because it was realized that the production of isooctane would be expensive and might be the bottleneck in the overall quantity of 100-octane gasoline that could be made. It was therefore desirable to keep the percentage of isooctanes in the final blend as low as possible. The octane numbers of the individual isohexanes and isoheptanes were studied and are tabulated. None have

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Solubility, gms/100 gms solvent	
Nitrobenzene	26.6 at 20°C
Orthonitrobenzene	22.6 at 20°C
Heat of Solution	550 small cal./gm. min.
Description	Gray, crystalline solid in three sizes
Analysis	
Aluminum Chloride	99% Min.
Iron	0.1% Max.

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octane numbers less than 73. Hence by removing the normal hydrocarbons an octane rating equal to 73 or greater could be obtained. For the production of a valuable cut it is necessary to separate between n-pentane and cyclopentane, at the front end, and between 3-methylpentane and n-hexane at the high boiling end. Eight fractionating units were built with 12-foot diameter columns, four being fitted with 50 trays, two with 76 trays, and two with 100 bubble trays. Seventy-six and 100 plate columns were built as two columns so that there were 12 columns in all varying between 120 and 140 feet in height. Data secured in the course of the research work are presented in considerable detail, and in part 2 of the article the production of isoheptane and isohexane at Abadan are described, and actual plant operating conditions are given. A flowsheet of the equipment is included.

Autoclave for Visual Observation of High Pressure Reactions. W. F. CALDWELL, *Ind. & Eng. Chem.* **38** (1946) pp. 572-75.

The trend toward high pressure and high temperature chemical reactions has made desirable the development of experimental apparatus permitting visual observation during the entire operation of the equipment. The author achieves this result by using a rotating Jerguson gage with clear glass on two sides. This is housed in an insulated casing, provided with strip heaters for raising the temperature and fitted with glass windows that permit reading of the temperature and pressure. The apparatus serves as a small autoclave, and can also be used for determining solubilities in solvents that are volatile at atmospheric pressure. Solution densities under varying conditions of temperature and pressure can also be measured. Detailed drawings of the equipment are given, and the apparatus is carefully described.

How to Use Metering Characteristics of Steam Jet Ejectors. P. FRENEAU, *Chem. & Met. Engr.* **53** (1946) pp. 104-7.

Although apparently simple devices, the characteristics of steam jet air ejectors are not well understood by many engineers, nor is it generally realized that when an ejector is operating stably it can be used as a metering device to determine the flow of vapor being drawn from an evacuated space. To accomplish this it is only necessary to measure the suction pressure and read the discharge rate from the characteristic curve of the jet. The author explains the operation of a jet. Although apparently simple in design, all parts of the jet must be carefully designed, machined and assembled. The relative position of the parts is critical; for example, the omission of the gasket between the nozzle plate and the mixing chamber, or the use of a thicker gasket, would seriously change the characteristic of the device. The economic compression range of a single jet is approximately 10:1. Typical ejector performance curves are presented and discussed. The use of a precondenser of direct contact or surface type will usually show large operating savings. A surface condenser is justified only when the condensable material has money value. Jets can be constructed of many different materials; for example, in handling corrosive vapors it is possible to use graphite. In general, ejectors are custom-built for the particular job they are to perform. The design involves at least

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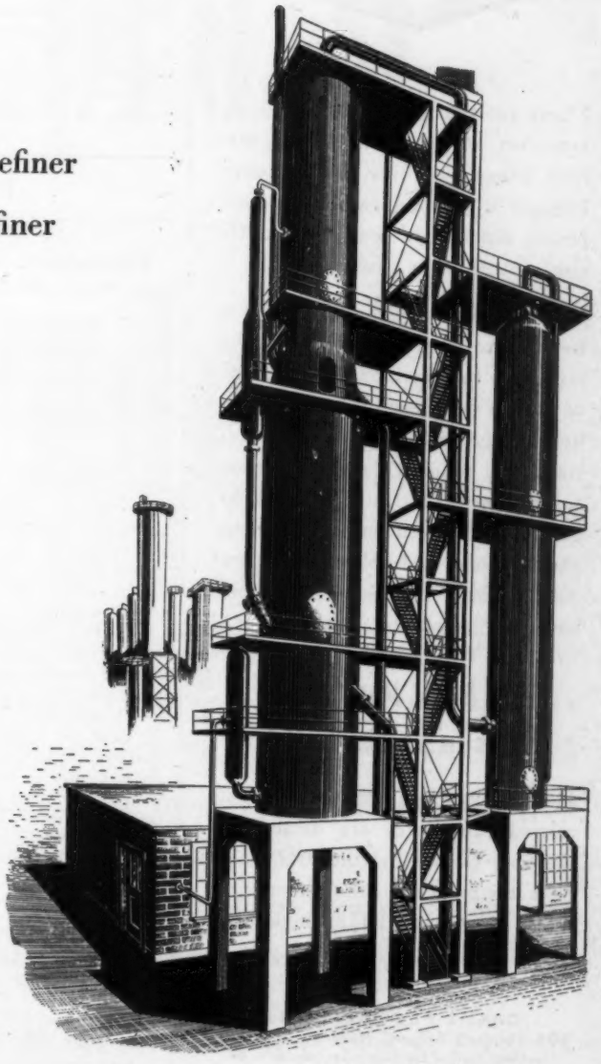

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14 variables, so really "standard" machines are impractical. In order to properly specify a unit, the capacity, absolute suction and discharge pressures and the minimum steam pressures should be given. Suction and discharge lines of generous size should be used to minimize pressure drop. An ejector does not work well with wet steam so a separator should be installed to eliminate moisture in the steam.

Metals and Alloys in the Petroleum Industry. J. H. WILSON, *Jour. Inst. Petr.* **32** (1946) pp. 230-240.

The author discusses the various metals and alloys useful to the petroleum industry, starting with mild steel, and continuing with high tensile steels, medium alloy steels, and stainless steels. Recent developments in the petroleum industry have taxed the ingenuity of metallurgists and much remains to be accomplished. The high chromium, high nickel alloys are briefly discussed in relation to such problems as the reversing factors in catalytic cracking furnaces and the use of these alloys as tube supports. Cast iron and alloy cast iron are briefly considered. The subject of non-ferrous metals is reviewed, particularly in their utilization as the metal of tubes and for the making of safety tools. The author stresses the necessity for the forging or pressing of safety tools, particularly those such as spanner wrenches, and emphasizes that cast tools should not be used. Also, the surface of soft metal tools can readily become loaded with particles of silica that may cause sparking if they come in contact with steel objects.

Nomograph for Formulas Containing Fractional Exponents. W. H. BURROWS, *Jour. Inst. Petr.* **32** (1946) pp. 256-68.

The author referred to a nomograph previously presented by McMillen for evaluation of fractional powers of terms and for the direct accumulation of a product of odd-power terms. Empirical formulas are frequently encountered that require the simultaneous involution of terms to fractional powers and multiplication or division of several such terms. The author has derived a new nomograph that accomplishes these results and in general requires fewer operations and is simpler in manipulation than the previously available chart. Changes were made that lead to greater accuracy of reading and interpolation of the scales and to a wider range of products. The use of the nomograph is illustrated by the solution of several typical problems.

Products: Properties and Utilization

Petroleum in Wartime. F. H. GARNER, *Jour. Inst. Petr.* **32** (1946) pp. 256-68.

The author reviews technical developments in the petroleum industry in wartime in many different fields, and including such products as aviation gasoline and antiknock agents, aromatic hydrocarbons, hydraulic oils for use in aircraft control, fuels and lubricants for land transport, flame-throwers and artificial fogs, smoke screens, asphaltic bitumens and plastic armour, bituminous emulsions and paints for blackout work, solvent extracts for camouflage, prefabricated bitumen surfacing for roads or air fields, waxes for waterproofing surfaces, rust preventatives, and many other products. The functioning of Great Britain as a base for the European conflict is briefly reviewed and described. The treatment of gasolines in storage to render it unsuitable for use by the enemy in case of capture of the stock is described. Use of petroleum products for defense, as in the Molotov cocktail, and in a static pipe system producing a continuous sheet of flame is reviewed. The Land Flame Barrage and the Sea Barrage are briefly described. The ignition of oil on water was studied in great detail and is considered by the author. The development of flame-thrower fuel is described. Incendiary bombs of various types are briefly considered.

The Char Value of Kerosine. F. W. H. MATTHEWS AND W. H. THOMAS, *Jour. Inst. Petr.* **32** (1946) pp. 269-88.

The paper summarizes the development of the Burnnig Test for kerosine and describes investigations into the reproducibility of the test when carried out in accordance with I. P. method 10/44 (T). The work indicates that the reproducibility of the char values by this method may not always be of the order claimed, and improved reproducibility can be obtained by the use of wicks extracted successively with water, alcohol, and petroleum ether. Data are given for a number of kerosines showing the reproducibility of the char value as determined by the standard method. Steps taken in an effort to improve the test are described, and details of experiments are given. With the exception of the properties of the wicks, none of the variables connected with the test greatly influences the values determined. Experiments using extracted wicks suggest the desirability of modifying the standard test.

The Mechanical Testing of Extreme Pressure Lubricants (with Special Reference to Hypoid Oils). H. L. WEST, *Jour. Inst. Petr.* **32** (1946) pp. 206-229.

The paper was prepared at the request of the Mechanical Tests for Lubricants Panel of Sub-Committee No. 5 of the Standardization Committee of the Institute of Petroleum. The paper covers details of the test procedure and research work on the five most used machines, and also gives specification tests and specifications that call for these particular tests. The lubrication of rear-axle drives was particularly studied, and the relation of the testing machines to this particular usage of them is emphasized. Modifications of the machines to bring them more into line with practice are indicated. The machines studied were: Almen, Timken, Four-ball, Falex, and S.A.E. machines. A bibliography of 48 references is included.

Rust Preventive Oils. G. P. PILZ AND F. F. FARLEY, *Ind. & Eng. Chem.* **38** (1946) pp. 601-9.

The economic loss due to rusting of iron and steel in service is extensive Early practice made use of grease and petrolatum when a removable coating was required. Coatings of oil, although more desirable from the standpoint of ease of removal, were not widely accepted as satisfactory until it was demonstrated that the rust preventive ca-

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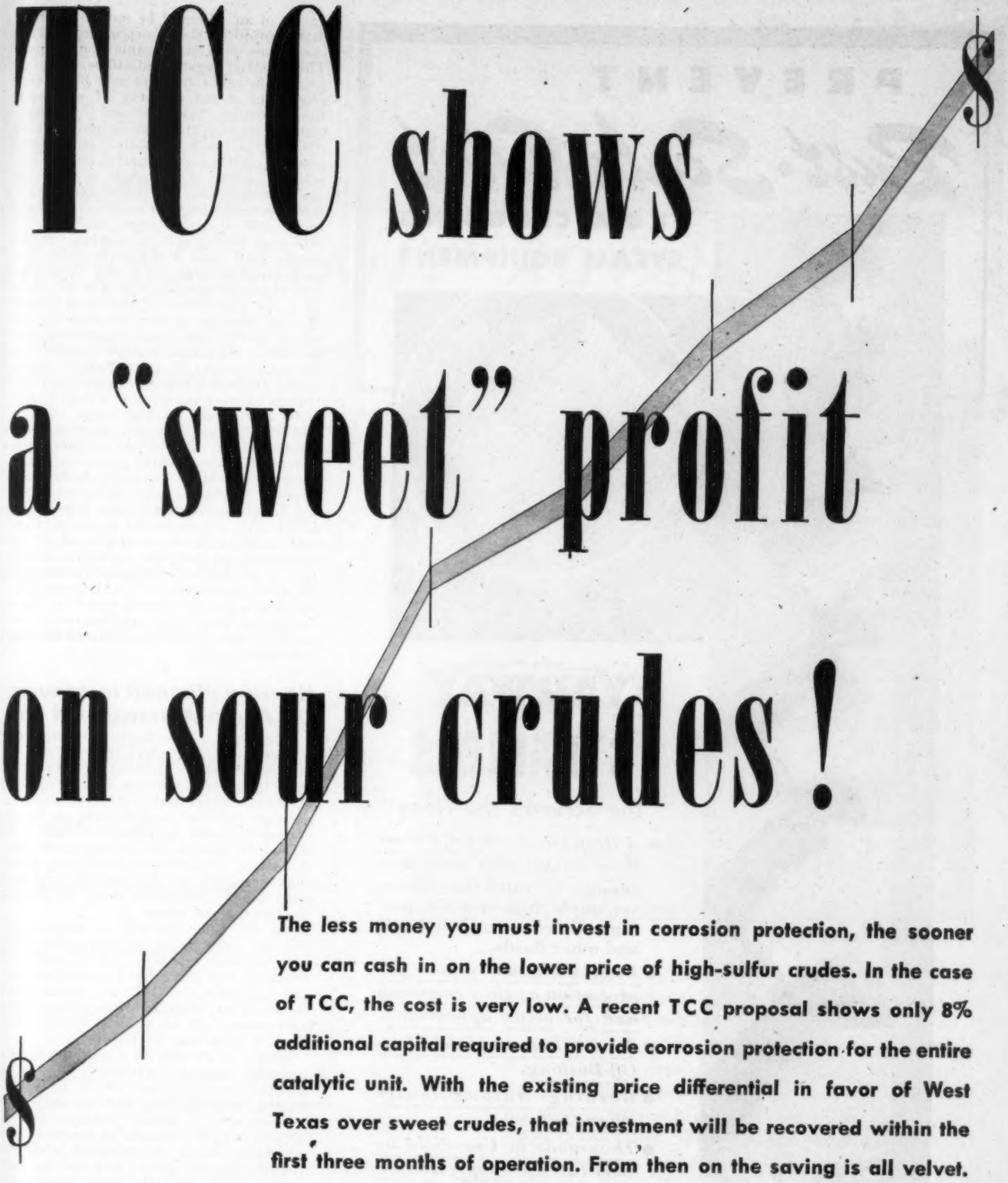

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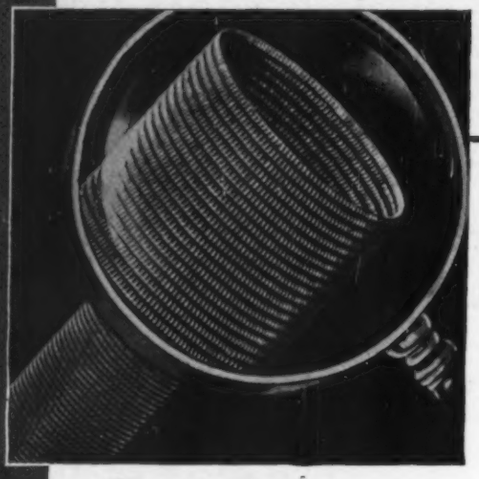

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pacity of an oil could be increased more than tenfold by the incorporation of certain types of polar organic compounds. These polar organic additives, such as petroleum sulfonates, are now being employed in a wide variety of oils both for protective coatings and for lubricants. The condensation of moisture in droplets on such oil-coated steel parts produces a dynamic system composed of water, oil film, and metal. A study of the contact angles formed by such a system where a drop of water rests on a horizontal oil-coated steel panel has established a relationship between contact angles and rust preventive ability. A mathematical analysis of the forces involved in the spreading of a water drop on a rust preventive oil film showed that the equilibrium surface tensions of the water and oil and their interfacial tension were the major factors determining the magnitude of the contact angle. These findings are in agreement with the theory of rust prevention which postulates orientation of the polar organic additive at the oil-metal interface and establishment thereby of a barrier to a normal mode of entry of the causative agents of rusting, namely, water and oxygen. Contact angles were measured by the authors by use of a microscope fitted with a goniometer eyepiece. Contact angles have been employed in determining the fact that solubility in water is of first importance among the physical properties of rust preventive additives, and the measurement of these angles has also found application in controlling the plant production of rust preventive oils.

Hearing Planned in January On Anglo-American Oil Pact

Hearings on the Anglo-American petroleum agreement will be held by the Senate Foreign Relations Committee next January. Chairman Tom Connally of Texas expressed the view that no damage will be done by the delay in considering the agreement, which was signed September 24, pointing out that the State Department itself has asked that hearings on the pact be delayed until the $3,750,000,000 loan to Britain had been acted upon.

By the time the next Congressional session opens, many of the problems in international relations which now are pressing will have been smoothed out, and the Senate committee, which plans to hear everybody who has views on the agreement, will be able to devote such time to it as may be necessary.

There is no talk of including Russia in the original agreement, it being pointed out that any effort to do so would entail getting into entirely new negotiations. Connally believes that if Russia is to be brought in, the necessary negotiations can be initiated after the British pact is ratified and can be used as the basis for talks with Soviet officials.

Indiana Standard Building Products Line to Minnesota

Standard Oil Company (Indiana) plans immediate construction of a products line from its Whiting, Indiana, refinery to Moorhead, Minnesota, across Red River from Fargo, North Dakota. Minneapolis is on the route. The line will be 662 miles long, 10-inch for most of the way and the balance 8-inch pipe. Location of terminals and pump stations along the line have not been announced.

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REFINING

U.S.P. 2,400,515. Method of Purifying and Deoderizing Crude Oil. F. A. Kent and C. W. Patrick.

Crude oil is heated to approximately 110° F. and mixed with a readily flowing mixture of hydrated lime and water. After thorough agitation muratic acid is added and after continued agitation the mixture is separated according to the description in U.S.P. 2,378,-776.

U.S.P. 2,400,654. Method of Separating Hydrocarbons. T. A. Petry and H. K. Holm to Socony-Vacuum Oil Company.

Toluene is separated from non-aromatic hydrocarbons of similar boiling point by adding to the complex mixture an aqueous solution of methanol, containing about 40 percent water based on the charge of the complex mixture, distilling off the water, distilling off a constant-boiling mixture of methanol and non-aromatics and recovering a residue rich in toluene. Non-aromatics are recovered from the constant-boiling mixture by settling and the aqueous solution of methanol is recycled.

U.S.P. 2,400,732. Conversion of Hydrocarbons. G. B. Arnold to The Texas Company.

A naphtha containing aromatic and non-aromatic hydrocarbons is extracted with water or with a solvent consisting essentially of water at a temperature above 500° F. and below the critical temperature of the lowest-boiling hydrocarbon to be extracted and under sufficient pressure to maintain the solvent in liquid phase. Aromatic hydrocarbons are extracted. The raffinate phase is contacted with a metal halide isomerization catalyst at 160-300° F. to effect isomerization of paraffins in the presence of naphthene constituents of the mixture.

U.S.P. 2,400,802. Separation of Aromatic Hydrocarbons from Hydrocarbon mixtures. G. B. Arnold to The Texas Company.

Aromatic hydrocarbons are separated from mixtures containing them by extracting with a solvent comprising a mixture of water and an auxiliary substance soluble in the water at the temperature of extraction. Suitable agents are olefin glycols applied in amounts of 5-25 percent by weight of the water. The extraction is carried out at 450-525° F. under sufficient pressure to maintain liquid phase.

U.S.P. 2,400,985. Desalting Crude Oils. B. L. Evering and A. P. Lien to Standard Oil Company (Indiana).

Crude oil containing alkali metal chlorides and alkaline earth chlorides is contacted with liquid anhydrous HF in an amount and for a time sufficient to convert the chlorides to fluorides with the formation of removable HCl.

U.S.P. 2,400,986. Desalting Crude Oil. V. Voorhees to Standard Oil Company (Indiana).

Oils having more than 20 pounds of salt per 1000 barrels of oil are desalted and freed from water by treatment with a hydrogen fluoride and water azeotropic or constant-boiling mixture. An oil phase substantially free of water and inorganic salts is separated from an aqueous phase comprising HF, water and inorganic fluorides.

U.S.P. 2,401,114. Process for the Separation of Diolefins from Hydrocarbon Mixtures. W. A. Schulze and G. H. Short to Phillips Petroleum Company.

The preparation of a cuprous halide reagent to serve in the separation of diolefins from hydrocarbon mixtures containing close-boiling non-dioefinic hydrocarbons is described. Dry powder cuprous halide is mixed in the absence of any solution phase or impregnation or fusion operation, with fibrous non-absorbent materials which produce permeable cohesive mechanical mixtures of high activity and capacity, such as asbestos or cellulose fibers. No packing or channeling is observed during passage of the hydrocarbon fluids.

U.S.P. 2,401,636. Process for Reducing the Olefin Content of an Olefinic Distillate. V. Haensel and V. N. Ipatieff to Universal Oil Products Company.

The olefin content of an olefin-containing fraction boiling in the gasoline range is reduced by contacting the fraction with a catalyst comprising an association of silica and at least one compound of an element whose oxide is refractory, such as alumina, zirconia, magnesia, thoria, ceria, etc., at 400-650° F. without effecting substantial cracking and under sufficient pressure to maintain a substantial portion of the hydrocarbons in the liquid phase. A liquid hourly space velocity of 0.3-15 is employed. The resulting gasoline fraction has a bromine number less than one half that of the charge stock.

U.S.P. 2,401,678. Removal of Hydrogen Halides from Hydrocarbon Conversion Products. G. B. Zimmerman to Universal Oil Products Company.

Hydrogen halide is removed from the reaction products of a hydrocarbon conversion process employing a hydrogen halide by fractionating the reaction products to separate a major portion of the hydrogen halide from the hydrocarbon, separating the residue into a fraction containing converted hydrocarbons and substantially all of the remaining hydrogen halide and a fraction containing the unconverted hydrocarbons. The former fraction is caustic treated to remove the hydrogen halide.

U.S.P. 2,401,758. Elimination of Acetylenes from Diolefins. S. H. Hastings and B. B. Turner to Standard Oil Development Company.

A hydrocarbon mixture having diolefins and acetylenes present therein is subjected to dehydrogenating conditions maintained to cause substantial destruction of the acetylenes without destroying appreciable amounts of diolefins. The diolefin content of the mixture is reduced to less than 3 percent by the addition of acetylene-free hydrocarbon diluent. Dehydrogenation is carried out in the presence of a catalyst comprising a major proportion of magnesia and minor proportions of Fe_2O_3, K_2O and CuO at a temperature of 1150-1300° F. and at a space velocity of 200-500.

U.S.P. 2,401,852. Solvent Extraction. G. B. Arnold and H. V. Atwell to The Texas Company.

Toluene is separated from a naphtha containing also non-aromatic hydrocarbons including olefins by counter-currently contacting a hydrocarbon fraction boiling between 212-242° F. with a solvent consisting of water containing about 20 percent ammonia in the ratio of about 5-20 volumes of solvent per volume of hydrocarbon at 425-450° F. and under elevated pressure not exceeding 1300 psi. The toluene content of the extracted hydrocarbons in the extract phase is about 99 percent by weight.

U.S.P. 2,401,896. Removal of Alpha Acetlyenes. W. C. Asbury and M. W. Swaney to Standard Oil Development Company.

Alkyl alpha acetylenes are separated from hydrocarbons containing butadiene by extracting the hydrocarbon mixture with a basic cuprous salt solution containing an amine which is volatile below 150° C. Excess amine is added to the extract which is heated to expel the alkyl alpha acetylene and excess amine. Instead of the solvent described a mixture of 3 mols per liter of cuprous ion, 4½ mols per liter of ammonia and 5½ mols per liter of ammonium acetate may be used as solvent.

U.S.P. 2,401,957. Stabilization of Petroleum Hydrocarbons. C. J. Pedersen and R. O. Bender to E. I. duPont de Nemours & Company.

A deterioration inhibitor is described, consisting of a 2-aminomethyl-4-aminophenol in which 1 to 2 amino hydrogens of the aminomethyl group are substituted by alkyl groups and 0 to 2 amino hydrogens of the 4-amino group are substituted by alkyl groups.

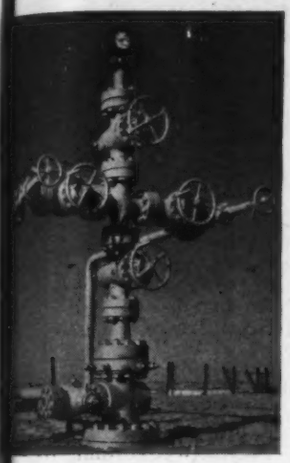
U.S.P. 2,401,983. Motor Fuels. A. L. Stanly and A. G. Cattanco to Shell Development Company.

A motor fuel for super-charged spark-ignition engines is described which consists of a major amount of a blend comprising 10-30 percent aromatics and 90-70 percent non-aromatics, the major portion of which is a trimethyl pentane fraction boiling between 105 and 115° C.

U.S.P. 2,402,113. Stabilization of Butadiene. L. F. Hatch, D. E. Adelson and B. O. Blackburn to Shell Development Company.

The polymerization of butadiene is

ENTIRE OIL INDUSTRY



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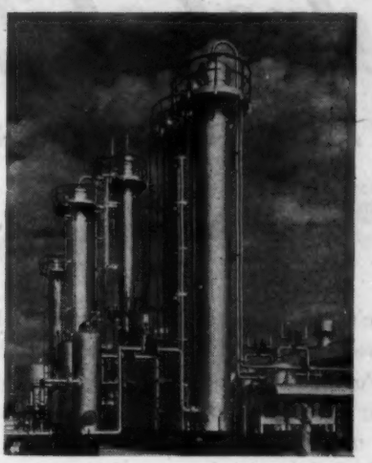

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- Prefabricated Piping
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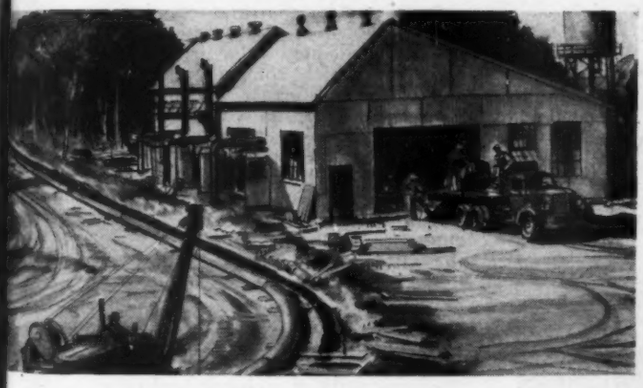

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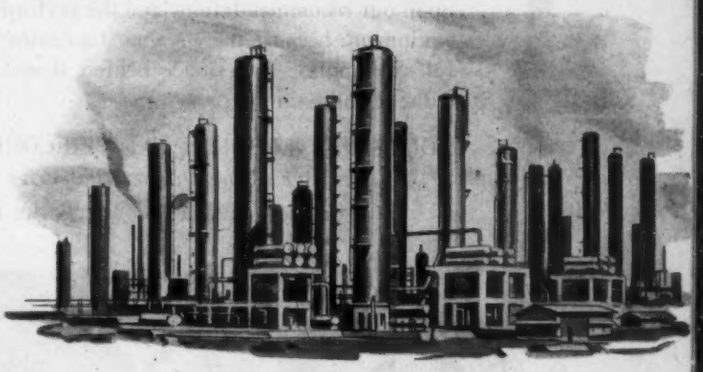

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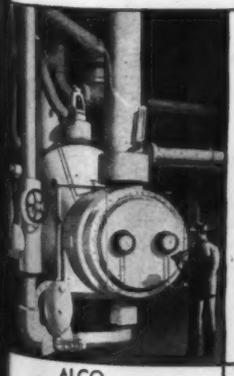

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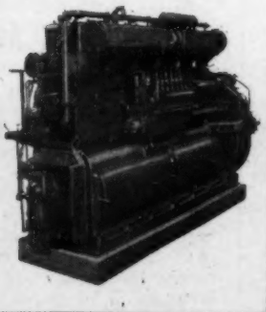

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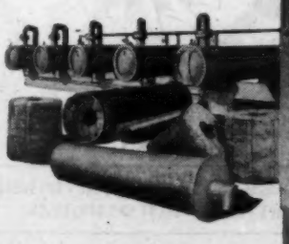

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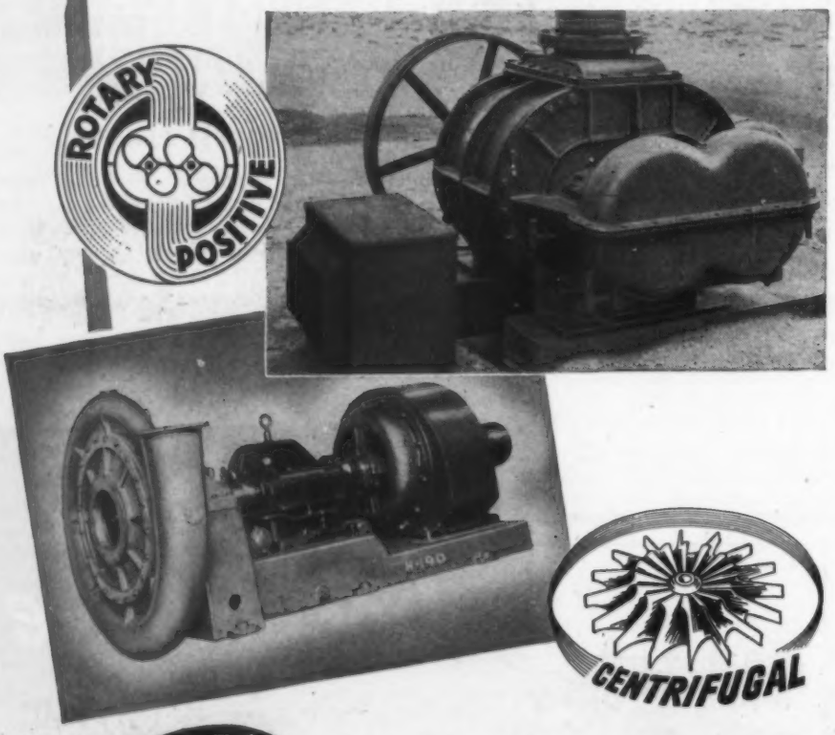

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CRACKING AND REFORMING

U.S.P. 2,401,363. Cracking Process. H. H. Meier to Standard Oil Development Company.

Gasoil is catalytically cracked at 850-1000° F., the cracked products are separated and a naphtha fraction obtained in the cracking process is passed to a thermal cracking zone maintained at 1000-1300° F. A naphtha fraction boiling between 200-400° F. is recovered from the products of the cracking zone and is treated with sulfuric acid to form a finished aviation-grade naphtha.

U.S.P. 2,401,649. Production of Aromatics. F. W. Ieffer to Universal Oil Products Company.

A combination cracking, aromatization and deolefinication process is described.

U.S.P. 2,401,865. Polymer Reforming. M. H. Gorin, E. Gorin, L. G. Sharp and I. H. Welinsky to Socony-Vacuum Oil Company.

A process for the production of liquid hydrocarbons of high octane number and low acid heat value from olefins is described which comprises passing the olefin in admixture with from 2-6 mols of a light i-paraffin (with from 4-6 C atoms) per mol of olefin in contact with a catalyst comprising an association of an acidic oxide and an amphoteric oxide, which has been subjected to an acid environment in the final stages of its preparation and in which the ratio of acidic oxide to amphoteric oxide is within the range of from 500:1 to 5:1, at a temperature between 275-500° C., at a pressure in excess of 100 psi and for a period of time sufficient to form liquid hydrocarbons consisting predominantly of aromatic hydrocarbons and saturated paraffin hydrocarbons from the olefin.

U.S.P. 2,402,034. Hydrocarbon Conversion. H. O. Folkins and C. M. Thacker to The Pure Oil Company.

Bromine substituted cyclic compounds in which bromine is attached to one carbon in the cyclic nucleus, regardless of the presence or absence of bromine in an alkyl side chain are very effective in the decomposition of hydrocarbons. Hydrocarbon oil is e.g. cracked to hydrocarbons of gasoline boiling range at 650-1400° F. in the presence of 0.1-5 percent of p-dibromo-benzene.

ISOMERIZATION

U.S.P. 2,400,669. Isomerization of Paraffinic Hydrocarbons. U. Tsao to The Lumnus Company.

Paraffin hydrocarbons are isomerized in the presence of an $AlCl_3$ catalyst by passing the vapors in contact with $AlCl_3$ under conditions permitting the $AlCl_3$ to gradually vaporize. The reacted vapors are passed to a scrubber and brought in contact with an $AlCl_3$-hydrocarbon sludge formed in the reaction zone. The sludge removes all entrained and vaporized $AlCl_3$ from the reaction products. The sludge is then contacted with fresh incoming paraffin vapors in a stripper. The vapors remove entrained

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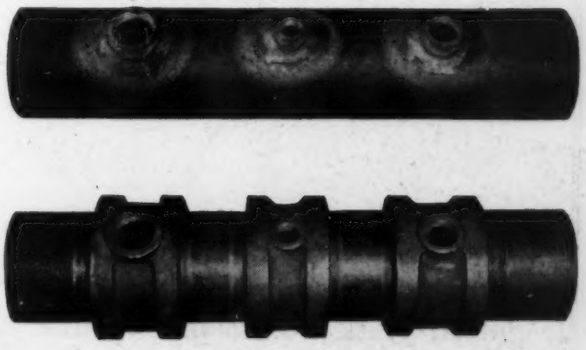

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or dissolved $AlCl_3$ from the sludge and carry it to the reaction zone.

U.S.P. 2,400,795. Hydrocarbon Conversion Process. C. W. Watson to The Texas Company.

Olefinic hydrocarbons contained in a gasoline fraction are subjected to catalytic isomerization by contact with an alumina catalyst at 700-800° F. for about 5 seconds. The resulting isomerizate is reacted under hydrogen transfer conditions with cyclic hydrocarbons containing alicyclic methylene groups. Hydrogenation of the olefins and dehydrogenation of the cyclic hydrocarbons occurs in the presence of a molybdena catalyst at 800-900° F. under 100-600 psi pressure.

U.S.P. 2,401,242. Process for Hydrocarbon Conversion. K. H. Hachmuth and D. G. Blaker to Phillips Petroleum Company.

Hydrocarbons to be isomerized are contacted with a sludge-forming metal halide catalyst of the Friedel-Crafts type. Effluent from the reaction zone is contacted in a second reactor with sludge formed in the first reactor to effect further isomerization and to remove volatile metal halide from the hydrocarbons.

ALKYLATION

U.S.P. 2,400,774. Process for the Production of Styrene and Butadiene. G. A. Nesty and W. C. Klingelhoefer to The Solvay Process Company.

Benzene and ethylene are reacted in the gaseous phase at a temperature between 775-850° C. and at a space velocity from about 75 to about 700 reciprocal hours, the mol ratio of ethylene to benzene introduced into the reactor being such that an excess of ethylene is present and preferably being between about 1.3 and 2.3. Styrene is produced in one step and appreciable quantities of butadiene are recovered from the reaction mixture.

U.S.P. 2,401,859. Manufacture of Gasoline Hydrocarbons. L. A. Clarke to The Texas Company.

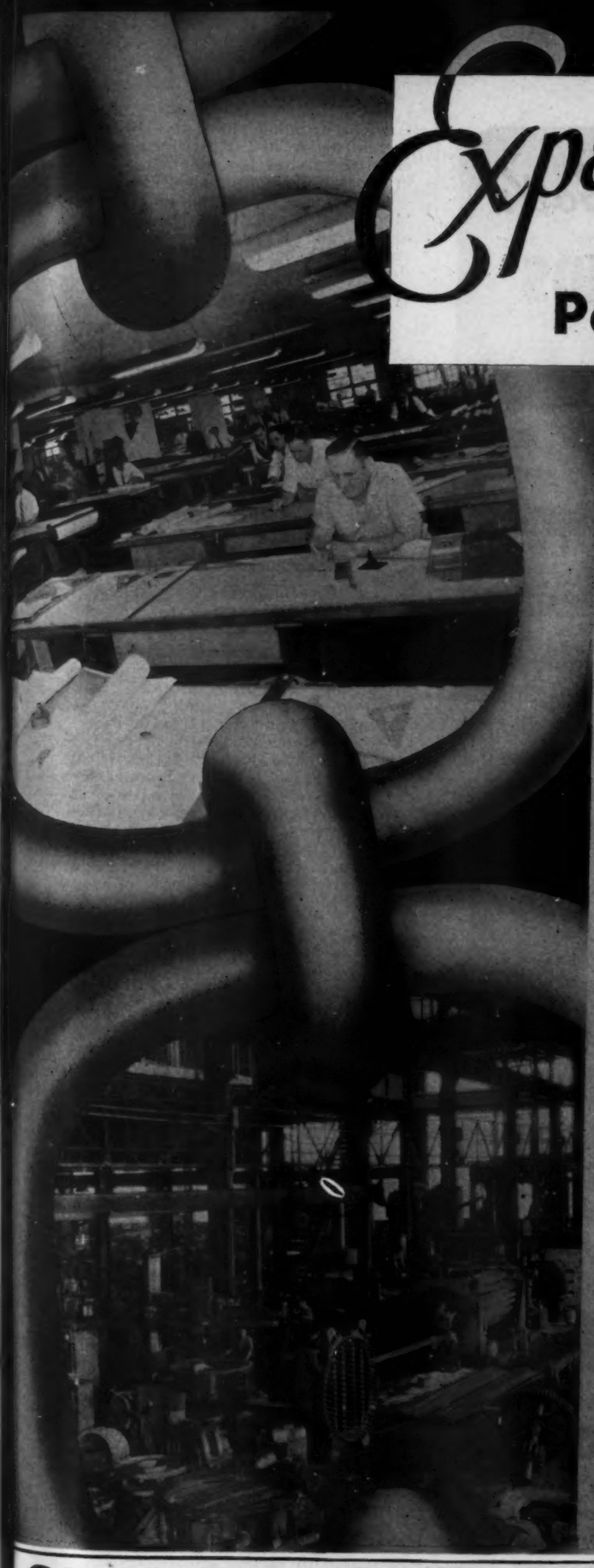
Propylene-free ethylene is alkylated with i-butane in the presence of an aluminum halide-hydrocarbon complex. After the efficiency of the alkylation catalyst is reduced beyond utility, the catalyst complex is employed in the isomerization of n-butane to i-butane. After the catalyst complex becomes spent for this reaction it is used to pretreat fresh ethylene feed, polymerizing and removing propylene from the feed stock.

U.S.P. 2,401,884. Alkylation Process and Catalyst Therefor. W. A. Schulze and W. N. Axe to Phillips Petroleum Company.

The alkylation of low-boiling isoparaffins with aliphatic olefins having at least 3 C atoms is carried out in the presence of a pretreated catalyst consisting of BF_3-phosphoric acid complex, BF_3 hydrate or mixtures of BF_3 hydrate with HF at a temperature from atmospheric to 150° F. The catalyst is pretreated with non-alkylatable hydrocarbons containing ethylene under conditions such that the ethylene combines chemically with the catalyst.

U.S.P. 2,401,925. Alkylation. M. H. Gorin to Socony-Vacuum Oil Company.

Hexane 2, 3 dimethyl butane is produced by alkylation of iso-butane and



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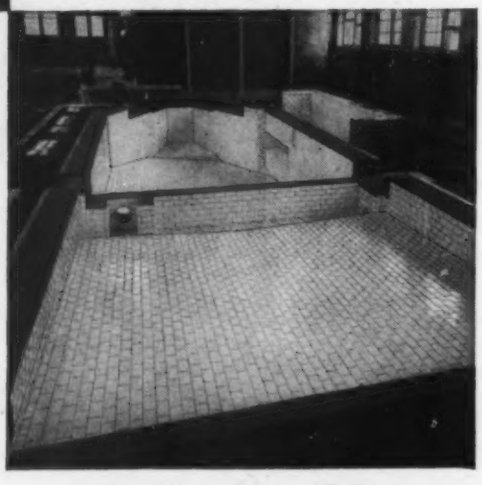

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ethylene in liquid phase at —10 to 70° C. and under 20-250 psi pressure. The effective catalyst is a solution of $AlBr_3$ in a paraffinic hydrocarbon. The $AlBr_3$ concentration in the solution is maintained between a catalytically effective amount and not more than 3 mol percent on the basis of total paraffin hydrocarbons in the reaction zone.

U.S.P. 2,402,092. Treatment of Aromatic Hydrocarbons. L. Schmerling and A. M. Durinski to Universal Oil Products Company.

A process for producing alkylated aromatics is described in which an alkyl halide is contacted with a molar excess of an aromatic hydrocarbon at 100-500° C. in the presence of a catalyst consisting of silica. In the case of alkylation of benzene, 1-20 mols of benzene are contacted with 1 mol alkyl halide under atmospheric —200 atmospheric pressure.

POLYMERIZATION AND CONVERSION

U.S.P. 2,400,520. Polymerization of Propylene. C. S. Kuhn, Jr., to Socony-Vacuum Oil Company.

Propylene in an amount of 16⅔ to 200 parts is contacted with 100 parts of hydrofluoric acid of 90-100 percent concentration at a temperature of 10-200° C. for a period of 30-180 minutes. Propylene is polymerized and at the same time hydrogen exchange occurs between the propylene polymers, forming saturated hydrocarbons and terpene-like unsaturated hydrocarbons. The former are recovered from the hydrocarbon phase, the latter from the acid phase.

U.S.P. 2,400,521. Olefin Polymerization. C. S. Kuhn, Jr., to Socony-Vacuum Oil Company.

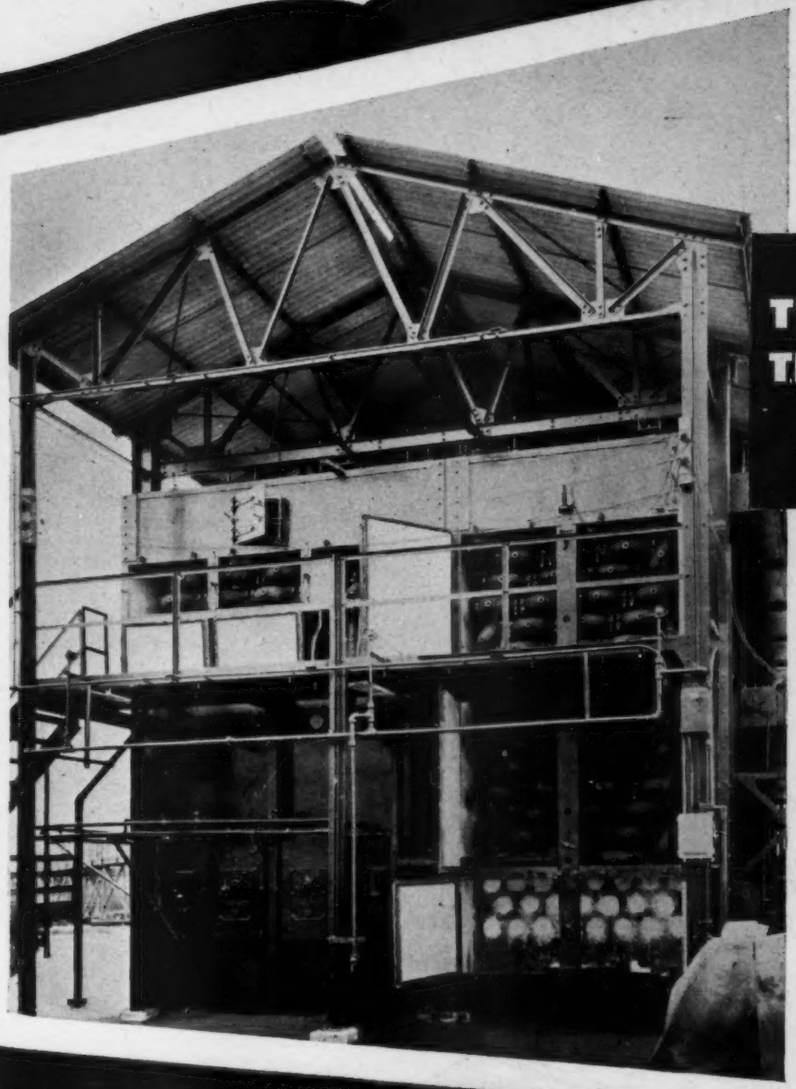
The process described in U.S.P. 2,400,520 is applied to olefins containing more than 3 C atoms per mol.

U.S.P. 2,400,621. Treatment of Hydrocarbon Gases. J. G. Alther to Universal Oil Products Company.

Olefins from a C_3-C_4 fraction are catalytically polymerized at a temperature below 550° F. and the polymerization product is stabilized. Liquid product is withdrawn and a portion of the normally gaseous product which is lean with respect to its content of higher olefins is recycled to the polymerization step, whereby a predetermined concentration of higher olefins is maintained in the reaction zone.

U.S.P. 2,400,922. Hydrocarbon Conversion System. B. L. Evering and E. L. d'Ouville to Standard Oil Company (Indiana).

The method of increasing the yield of high-antiknock aviation-gasoline stocks from light paraffinic hydrocarbons which method comprises fractionating said hydrocarbons to obtain a light normally gaseous fraction, a heavy normally gaseous fraction, reacting said light normally gaseous fraction with steam for the production of hydrogen contaminated with carbon monoxide, polymerizing hydrocarbons in said heavy normally gaseous fraction to produce a polymer of the aviation-motor-fuel boiling range, hydrogenating said polymer with said hydrogen under conditions for effecting a substantial reduction in the carbon monoxide content of the un-



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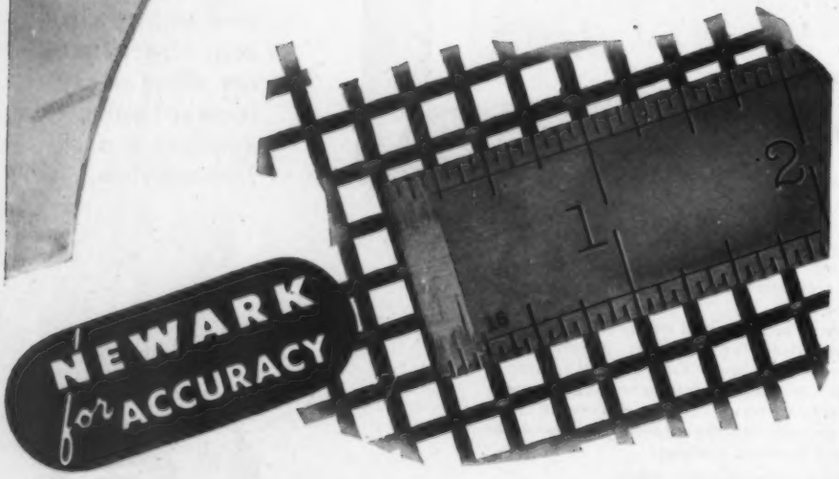

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consumed hydrogen, isomerizing the light normally liquid hydrocarbons with a halide isomerization catalyst under isomerization conditions in the presence of added hydrogen and under a substantial hydrogen pressure, utilizing at least a portion of the unconsumed hydrogen from the hydrogenation step for supplying the added hydrogen to said isomerization step, and blending hydrogenated polymer and isomerized light normally liquid hydrocarbons from the hydrogenating and isomerizing steps respectively to produce high-antiknock aviation-gasoline stocks.

U.S.P. 2,401,414. Diene Dimer. T. F. Doumani and R. Deery to Union Oil Company of California.

Butadiene, isoprene or cyclopentadiene are converted to their dimers by passing mixtures containing the dienes together with mono-olefins and other hydrocarbons downward through a vertical reactor having a surface to volume ratio below 100 square feet per cubic foot at 400-600° C., under 50-1000 psi pressure at a rate permitting a contact time of less than 5 seconds and sufficient only to attain a maximum conversion of less than 50 percent of the dienes present.

U.S.P. 2,401,754. Production of Polymers. A. D. Green to Standard Oil Development Company.

Polymer, prepared from an iso-olefin at temperatures below —40° C. in the presence of a Friedel-Crafts type catalyst is discharged into a heated liquid medium as a slurry of polymer in cold low-boiling reaction liquids. Low-boiling reaction liquids are flashed off and polymer is then separated from the liquid and dried in a drier.

U.S.P. 2,401,922. Process for Thermally Reacting Hydrocarbons. F. E. Frey, H. J. Hepp and G. H. Morey to Phillips Petroleum Company.

Normally gaseous paraffin hydrocarbons heavier than methane are reacted to form higher-boiling hydrocarbons by scission and polymerization, the reaction being promoted by admixing ethylene oxide (in amounts of not more than 10 mol percent) with the hydrocarbons. The reaction is carried out under temperature and time conditions which would undesirably limit such reaction if unpromoted.

HYDROGENATION DEHYDROGENATION AROMATIZATION

U.S.P. 2,400,843. Process for the Manufacture of Aviation Gasoline. W. A. Schulze and C. J. Helmers to Phillips Petroleum Company.

A cracked-gasoline charge stock is aromatized by passage over a bauxite catalyst at 1050-1250° F. at a liquid space velocity of 0.5-10 and under up to 200 psi pressure. The product is cut into three fractions, boiling to 200° F., from 200-350° F. and above 350° F., respectively. The highest-boiling fraction is recycled. The other two fractions are subjected separately to polymerization with a silica-alumina catalyst at 200-600° F. under 500-2000 psi pressure. Aviation-gasoline stock boiling between 200-350° F. and a bottoms product which is recycled to aromatization are recovered. The silica-alumina catalyst

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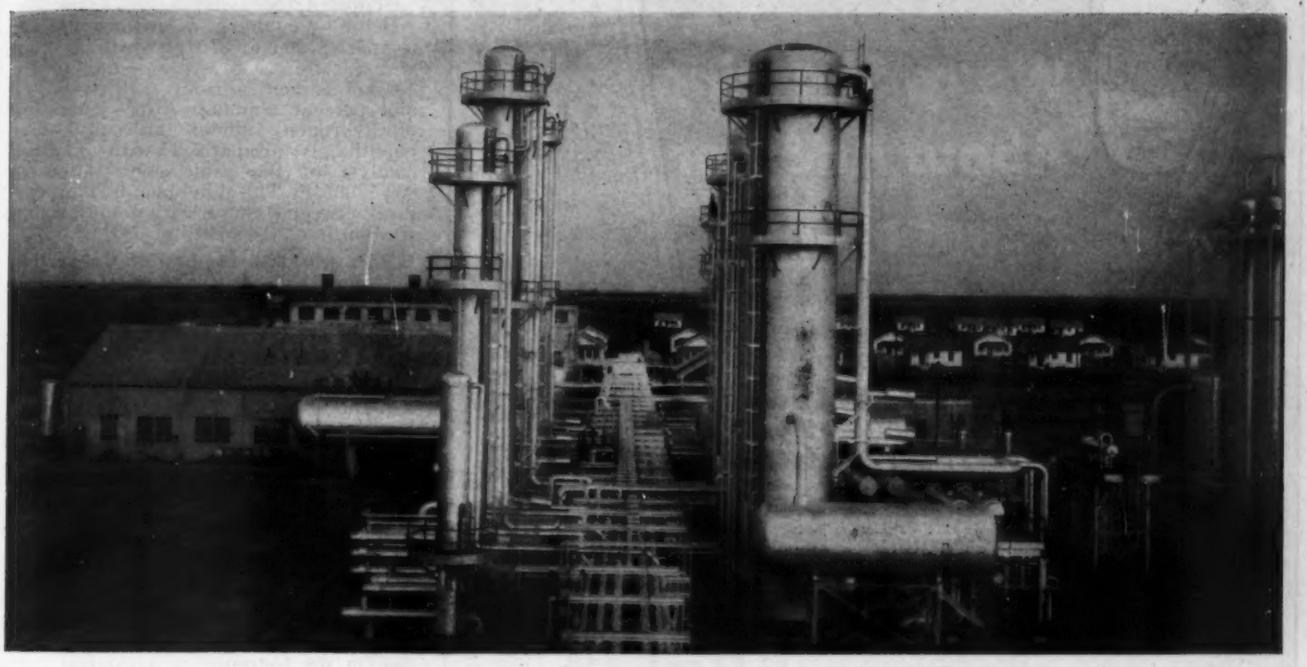

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comprises silica and from 0.1 to 2 weight percent of alumina.

U.S.P. 2,401,334. Process of Aromatizing Sulphur-Containing Hydrocarbons. R. E. Burk and E. C. Hughes to Standard Oil Company of Ohio.

Sulfur-containing hydrocarbons are treated at 200 to 850° F. with a spent aromatization catalyst consisting of 18-30 mol percent chromia gel and 70-82 mol percent alumina. After separation of hydrogen sulfide, the sulfur-free naphtha is aromatized with a fresh catalyst of the same composition at 800-1200° F. The difference in temperature between desulfurization and aromatization is of the order of 330° F.

U.S.P. 2,401,802. Method of Converting Mono-Olefins to Diolefins. H. S. Taylor and J. Turkevich to The M. W. Kellogg Company.

Mono-olefins are converted to diolefins by contact at elevated temperature with a solid granular catalyst, comprising alumina and particularly α-alumina impregnated with an oxide of a metal of the left hand columns of groups IV, V and VI of the periodic table. The reaction is carried out in a non-oxidizing atmosphere containing at least 1 mol of steam per mol of mono-olefin.

U.S.P. 2,401,846. Procedure for Olefin Dehydrogenation. S. D. Sumerford to Standard Oil Development Company.

Hydrocarbons are dehydrogenated at 1100-1300° F. in admixture with steam and in the presence of a catalyst consisting of approximately 19 percent Fe_2O_3, 72 percent MgO, 4.5 percent CuO and 4.5 percent K_2O. The catalyst is activated prior to use in dehydrogenation reactions by passing a mixture of steam and normally gaseous paraffin hydrocarbon over it.

U.S.P. 2,401,872. Production of Diolefins. J. P. Jones to Phillips Petroleum Company.

Butadiene is produced from C_3 and C_4 paraffins. The paraffins are dehydrogenated to the corresponding olefins, which are subjected to 1300-1700° F. and a low pressure for a time such, that 3-10 percent of butadiene and benzene are synthesized. Butadiene is separated and the benzene is hydrogenated with the hydrogen from the dehydrogenation step. Cyclohexane is converted to butadiene and ethylene at 1050-1550° F. Butadiene is separated and ethylene recycled.

U.S.P. 2,401,973. Dehydrogenation of Butylene and Pentylene. W. D. Seyfried and S. H. Hastings to Standard Oil Development .Company.

Butylene is passed over a dehydrogenation catalyst consisting of approximately 80 percent MgO, 14 percent Fe_2O_3, 3 percent K_2O and 3 percent CuO to produce butadiene. The reaction temperature is gradually raised from 1150-1300° F. After about .5 percent carbon has been deposited on the catalyst a pentylene feed stock is passed over the catalyst at 1150-1300° F. to produce C_4 and C_5 dienes until about 4 percent carbon has been deposited on the catalyst.

CATALYST PREPARATION ACTIVATION AND REGENERATION

U.S.P. 2,400,874. Recovery of Catalysts. R. E. Burk to The Standard Oil Company (Ohio).

HF and BF_3 each form a complex with or are absorbed by amines. The

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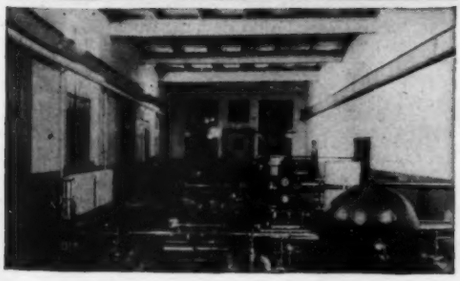

Above: Installation showing the use of Crouse-Hinds Type ADE heavy duty floodlight for general illumination, together with Type VAW obstruction lights for air markers.

Left: Installation showing the use of Crouse-Hinds Type ADE heavy duty floodlights outdoors, for lighting an interior in an extremely hazardous location where no electric wiring was used within the building.

Right: Installation of Crouse-Hinds Type ADE heavy duty floodlights on a steel tower for general illumination.

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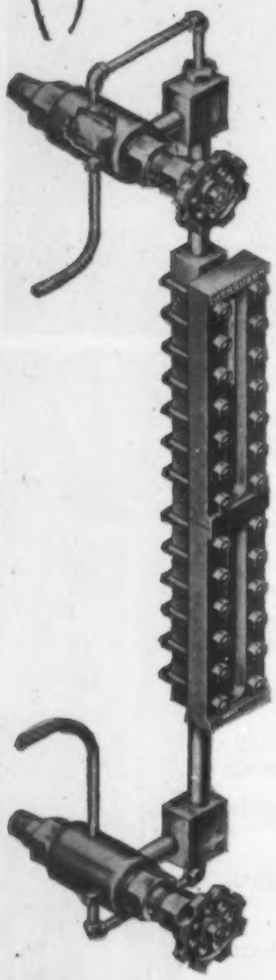

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complex absorption product can be disassociated by heating, releasing the unchanged fluoride from the amine. HF and/or BF_3 are separated from hydrocarbons by absorption in an amine and subsequent recovery of the fluoride from the amine.

U.S.P. 2,400,875. Absorption and Recovery of Fluorides in Amines of Low Basicity. E. C. Hughes and J. D. Bartleson to The Standard Oil Company (Ohio).

The process described in U.S.P. 2,400,874 is carried out, utilizing amines of low basicity as absorbents. These form less stable and easier disassociated complexes than amines of higher basicity. Amines of preferred basicity have a dissociation constant of the order of 1×10^{-10}, such as diphenylamine, ditolylamine, chloro- or nitro aniline, etc.

U.S.P. 2,400,959. Hydrogenation and Dehydrogenation Catalysts. M. M. Stewart to Iowa State College Research Foundation.

The catalyst which is effective in the hydrogenation and dehydrogenation of organic compounds at 100-300° C. and under 10-400 atmosphere in the presence of hydrogen consists of a major proportion of activated cuprous oxide which is easily wet by water, a small promoting quantity of alkaline earth metal oxide or hydroxide and vanadium oxide as a stabilizing agent. The cuprous oxide is prepared from cupric sulfate or nitrate solution by adding a weak reducing agent such as an aldehyde and 8-10 percent by weight of sodium hydroxide.

U.S.P. 2,402,051. Catalysts. V. N. Ipatieff and L. Schmerling to Universal Oil Products Company.

A catalyst for hydrocarbon conversion reactions is prepared by mixing an aluminum halide (such as $AlCl_3$) and a phosphoric acid (such as ortho-phosphoric acid) in approxmiately equimolecular proportions and heating the mixture (to 80° C.) until about 1 mol hydrogen halide per mol aluminum halide is evolved.

HEAVY OILS AND WAXES

U.S.P. 2,400,611. Turbine Oils. H. G. Smith, T. L. Cantrell and J. G. Peters to Gulf Oil Corporation.

An oil-soluble composite improvement agent is described which is readily soluble in turbine oils and imparts marked rust-preventing qualities to it. Used in quantities of 0.01 to 1 percent, the agent comprises a blended mixture of polyvalent metal salts of 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid with cyclohexyl amines and primary fatty amines, respectively.

U.S.P. 2,401,273. Mineral Oil Composition. O. M. Reiff and D. W. Andrus to Socony-Vacuum Oil Company.

An improved mineral oil composition is described comprising a viscous mineral oil and in admixture therewith a minor proportion, from about 0.1-5 percent, of an oil-soluble metal hydrosulfide of a basic polyvalent-metal salt of an alkyl-substituted aromatic hydrocarbon compound, said alkyl substitutent being an oil-soluble alkyl group.

U.S.P. 2,401,933. Polymerization of Olefins to Oily Polymers. A. B. Hershberger to The Atlantic Refining Company.

Lubricating oil is produced by polymerizing a mixture of 40-60 percent

Looking Around

By THE OBSERVER

EVER CHECK 36 SPARK PLUGS OF AN AIRPLANE ENGINE?

Ever go over the ignition of an 18-cylinder airplane engine?

It used to be something! The least hint of trouble called for almost endless checking. It took hours, even days.

At California Research Corporation, a subsidiary of Standard of California, there are some whiz-bang specialists in electronics. This problem was down their alley, so they tore after it.

They worked out an uncanny trouble-finding doodle-bug that they call an Ignition Analyzer. Hook it on and it checks all ignition parts simultaneously. It goes through that power plant and connections from rooter to tooter. It's all set up, does its work and bows out in half an hour, leaving word on exactly what part is at fault, and why.

Maybe you don't care a whoop how many hours that saves the transport company, though a tied-up plane can cost $500 an hour.

But it's pleasant to know that, when you go to take off, you may be saved hours of waiting time. Even though you are only plain John Q. Jones, trying to get somewhere to be bridegroom, say, at a wedding.

We won't claim for the Ignition Analyzer that it washes the plane, collects the tickets or puts a pillow under your head. But—and this goes for California Research Corporation in general, too—it does do the darndest things!

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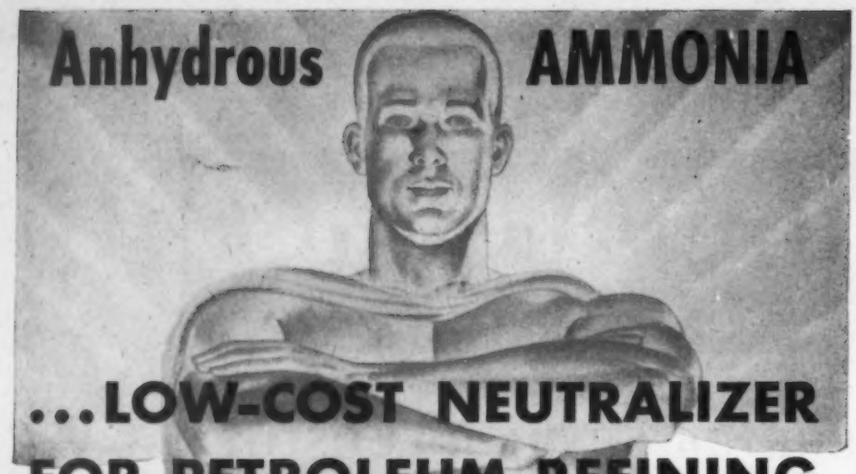

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propylene and 60-40 percent i-butylene. The mixture is cooled to —10 to 35° C. and sprayed with a cooled solution of $AlCl_3$ in a lower alkyl halide such as ethyl chloride, while being agitated vigorously. The hydrocarbon mixture may be diluted with alkyl halide prior to the addition of the catalyst solution.

Dr. Gustav Egloff Leaves For Lecture Series in England

At the invitation of the Institute of Petroleum of Great Britain, Dr. Gustav Egloff of Universal Oil Products Company, is to deliver a series of lectures before various local chapters of the institute in England, Scotland, and Wales. He also will lecture at Oxford and Cambridge universities, and will address the Catalyst Club of England, in London. His subjects are "Catalysis in the Oil Industry," "Petroleum as a Chemical Industry," and "Modern Products from Crude Oil."

He left Chicago August 5, by air, for London. On August 20 he will fly from London to Gothenburg, Sweden, to join a party of American scientists and technologists who will visit the universities and the centers of scientific and industrial research of the Scandinavian countries, at the invitation and under the auspices of the Royal Swedish Academy of Engineering Research.

Dr. Egloff expects to fly from Oslo, Norway, to Chicago on September 6 to attend the 110th annual meeting of the American Chemical Society in Chicago.

Jersey Standard Wins German Patent Suit

Standard Oil Company (New Jersey) has recovered 798 patents seized by the Alien Property Custodian during the war because of alleged German interests. A decree to that effect was entered by a federal court in New York. Under the order, attorneys estimated, the company retained "title or at least excusive licensing rights" to 70 percent of the patents, which were part of a $35,000,000 purchase from I. G. Farben Industrie in 1929 and 1939.

While rights to the principal buna rubber patents which were involved in the litigation were retained by the Alien Property Custodian, company attorneys declared that they had been granted, royalty free, to all manufacturers to expedite the synthetic rubber program. Other patents in the proceedings covered oil refining and hydrocarbon processing.

The company contended that no German interests in the patent rights remained after 1939, while the government maintained that the transfer of patents from the German company was a transfer in form only.

Edward H. Zeitfuchs Retires

Edward H. Zeitfuchs, senior physical chemist for California Research Corporation at Richmond, California, is retiring after 25 years with the organization. He joined Standard Oil Company of California in 1921, and specialized in measuring the properties of petroleum. He is the inventor of the viscosity meter bearing his name.

Zeitfuchs was graduated from the University of California in 1912 as bachelor of science, took his master's degree at Massachusetts Institute of Technology in 1918, and received his doctorate at Clark University in 1921.

NEW EQUIPMENT

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1—Diaphragm Control Valves

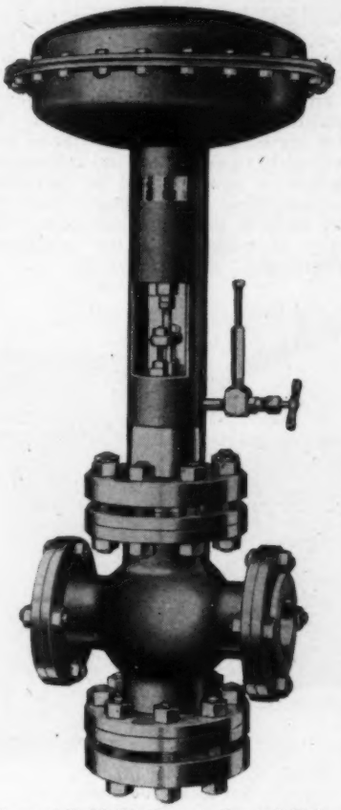
Hammel-Dahl Company, 243 Richmond Street, Providence 3, Rhode Island, is offering a full line of diaphragm control valves in sizes ½- to 1-inch in alloy construction, either in 304 or 316 stainless steel or other corrosion-resistant alloys obtainable in cast form.

A feature of these valves is the use of a single body casting for each size, this body construction being rated at 600 pounds maximum working pressure at 750° F., and also, in the use of split flanges giving a Van Stone type of joint for ASA pressure ratings of 150, 300 or 600 pounds.

Split flange construction eliminates the usual difficulty of obtaining sound castings in these alloys. An advantage of the split flange construction is that valves may be changed from point to point for use at different pressure ratings merely by replacing the removable flanges.

These valves incorporate all-steel diaphragm superstructure with two-ply neoprene diaphragm, valve position indicator, through-bolted stuffing glands, and stuffing-box lubricator and isolating valve. The standard air pressure operating range is 2-15 psi; other ranges are available. For high-temperature service, airfin bonnets are available.

CHECK THE CARD AT PAGE 249



Hammel-Dahl Diaphragm Control Valve

2—Swivel Pipe Coupling

Snyder Sales Corporation, 5225 Wilshire Boulevard, Los Angeles 36, has announced the All-Flex Ball-Bearing Swivel Pipe Coupling, designed to convey fluids under high pressure through a tube which swivels or rotates 360 degrees. It consists of male and female elements into which double ball races are cut. The double rows of bearings perform the dual function of locking the two elements together, as well as carrying the rotating and operating load between the swivel parts. Multiple metal-backed packings of synthetic packing material vulcanized to a metallic backer minimize the torque load and offer leak-proof and long-life service from 0 to 1000 psi. It is preferably made of steel and is available in sizes from ⅛- to 1-inch tube sizes with a variety of threaded and elbow connections. An informative booklet is available.

CHECK THE CARD AT PAGE 249

All-Flex Ball-Bearing Swivel

3—Water Analysis Kit

The Permutit Company, 330 West 42nd Street, New York 18, has announced a new kit for testing water for hardness, alkalinity and chlorine content. The kit, containing solutions and precision-made pippette droppers for accurate measurements, comes in a portable enameled cabinet, 10 x 10 x 4¾ inches. It can be modified to permit testing of sodium sulfite in water.

CHECK THE CARD AT PAGE 249

4—Pipe Tools

Beaver Pipe Tools, Warren, Ohio, has issued a condensed catalog of its pipe tools, including prices.

CHECK THE CARD AT PAGE 249

5—X-Ray Photometer

General Electric Company, Schenectady, New York, has announced a new X-ray photometer which indicates and records the concentration of one chemical element in the presence of others in solids, liquids or gases. The new instrument, which is nondestructive to most materials, accomplishes this by measuring the change in absorption of X-rays between a sample and a standard.

The X-ray photometer can be used in such applications as determining sulphur content of oil, lead content of gasoline, and bromine concentration in certain brominated compounds. Sensitivity of this method of analysis varies from 0.01 to 1 percent, depending upon the difference in atomic numbers of the components making up the specimens.

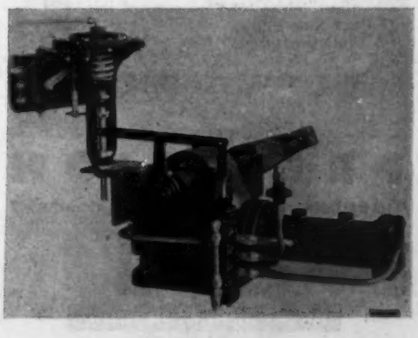
The X-ray photometer is housed in a standard control cabinet, 72 inches high, 28 inches wide, and 20 inches deep. The equipment incorporates a standard General Electric X-Ray Corporation industrial generator. The X-ray transformer and tube are oil-immersed. The tube has a beryllium window and a tungsten target, and is water-cooled.

All controls are available from the front of the cabinet. Provision is made for several types of test calls, in which the samples are contained, and the liquid and gas cells can be arranged for continuous flow of the materials being analyzed. The instrument features high speed of response and continuous operation. No special skill is required to operate the analyzer, and analysis is independent of temperature or pressure for solids and liquids.

CHECK THE CARD AT PAGE 249

6—Hydraulic Booster Cylinder

Askania Regulator Company, 1603 South Michigan Avenue, Chicago, has announced an oil-operated hydraulic booster cylinder for air operated controllers. Using a standard diaphragm top it provides high power amplification and



Crank Type Askania Hydraulic Cylinder

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permits exact positioning of heavy dampers, valves and the like in accordance with the applied pneumatic loading pressure—usually 0-15 pounds psi.

The cylinder may be of the crank type or of the straight reciprocating type. Straight cylinders are available up to 8-inch bore and 30-inch stroke.

Other types of remote positioning cylinders are available using electric instead of pneumatic transmission.

CHECK THE CARD AT PAGE 249

7—Chlorinator

Paddock Engineering Company of Texas, 900 South Ervay Street, Dallas 1, Texas, is marketing a portable high-capacity chlorinator which is claimed to be an efficient, safe and inexpensive method of introducing chlorine into water for cooling towers, boiler or other services. It operates on the full-vacuum principle, a new method of controlling chlorine. Float boxes, float valves and other moving parts are eliminated. Possibility of make-up water overflowing is eliminated.

Paddock Chlorinator

Parts coming in direct contact with chlorine are fabricated of silver, glass or hard rubber. Glass parts are enclosed in a steel cabinet for protection against breakage. The unit is light enough to be easily moved from location to location, and rugged enough to stand abuse.

The unit handles up to 1000 pounds of chlorine in 24 hours, with meter control within 4 percent. Capacity is easily changed in the field without special skill or experience.

A positive check valve prevents moisture backing into the machine and chlorine cylinder when not in operation. Another check valve and hose connection allows chlorine gas to bleed at atmosphere in case of injector water pressure failure.

CHECK THE CARD AT PAGE 249

8—Ketones

Carbide and Carbon Chemicals Corporation, 30 East 42nd Street, New York 17, has issued a booklet, Form 4767, which discusses physical and chemical properties of 10 commercially important ketones it produces. Specifications and shipping data are given, as well as information regarding principal uses of these products.

CHECK THE CARD AT PAGE 249

9—Thermal Protector

Manning, Maxwell & Moore, Inc., Bridgeport, Connecticut, announces a new Ashcroft Thermal Protector — a thermocouple-actuated limit switch.

As an example of its use, the manufacturer states that protection is required on bearings of large motors, blower wheels, flue gas stacks of boilers, etc. The temperature chosen as the high limit is set by an operating knob located inside the case. If this temperature is reached, the device will stop the apparatus before excessive damage is done, or it can be arranged to sound an alarm or light a light.

In addition to protection from excessive temperature, the device will "fail safe" in case of burning off or breaking the thermocouple, failure of power supply, tube or mercury switch.

Manual reset makes certain that something is done to correct the cause before the equipment is damaged or production is seriously interrupted.

The thermal protector is designed with two ranges, 100° F. to 1000° F. using an IC couple, and 800° F. to 2000° F. using an AC couple with an accuracy of 2 percent of the range at a set point. Two or more couples may be connected in series if desired. The cold junction is located in the unit and is compensated to ambient temperatures of 50° F. to 135° F. and a relative humidity up to 100 percent.

The current characteristics are 115-230 volts 60-cycle AC 15-20 watts. There are no open contacts in the device and the circuit for the signal and power input to the apparatus is a standard 4-amp. 250-volt mercury switch.

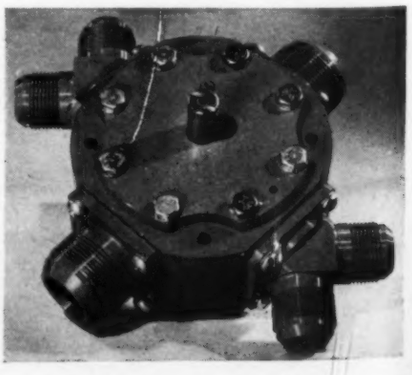
The case for this device is designed for universal mounting either flush or wall.

CHECK THE CARD AT PAGE 249

10—Selector Valves

Hydro-Aire, Incorporated, 626 North Robertson Boulevard, Los Angeles 46, has recently engineered and is now manufacturing a complete series of industrial two-way, three-way and four-way selector valves.

These valves are capable of handling flows up to 2500 gallons per hour with negligible pressure drop. Sizes range from ⅜ to 1½ inches. Units incorporate patented sealing methods which are also used in critical aircraft fuel valves. The features of these valves are: extremely light weight; low operating torque; not affected by back pressures; suitable for use at temperatures ranging from minus 65° F. to plus 200° F.; small size for large capacity of fluid handled; can be used for any type of liquid, and can be



Hydro-Aire Four-Way Selector Valve

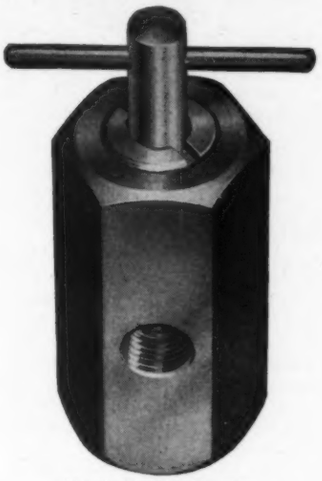
serviced easily by inexperienced personnel.

Valve can be positioned at 200 psi, and will withstand operating pressures of 1000 psi. A plug type design is used; thus, insuring fewer parts and lower cost. Unit can also be supplied in small sizes for use in compressed air lines.

CHECK THE CARD AT PAGE 249

11—Pulsation Damper

To protect gauges and recorders where surging pressures are exposed directly to pumps, compressors and steam lines, Martin-Decker Corporation, Long Beach, California, has developed a new packing arrangement for the Martin-Decker pulsation dampers.



Martin-Decker Damper

The manufacturers claim this new packing development requires no tightening; reduces stem friction; holds either vacuum or pressure; requires no gland adjustments and may be used for oil, gas or gasoline. These packings can be furnished for pressures up to 12,000 pounds and for temperatures up to 225° F. For temperatures exceeding 225° F. conventional asbestos packing is furnished.

The pulsation damper is designed for use on any pressure installation where readable indications and charts are required, such as pressure controllers, orifice meter U-tubes, draft gauges and many other types of pressure measuring instruments and pressure operated devices.

Effective control of surging pressures is accomplished by engagement of two taper threads. The stem is threaded with one type while the threads of the damper body are slightly dissimilar. During engagement these two dissimilar threads produce a small orifice around the thread lips. Simply by turning the damper stem inward or outward for pressure adjustment the spiral orifices between the threads are diminished or enlarged.

CHECK THE CARD AT PAGE 249

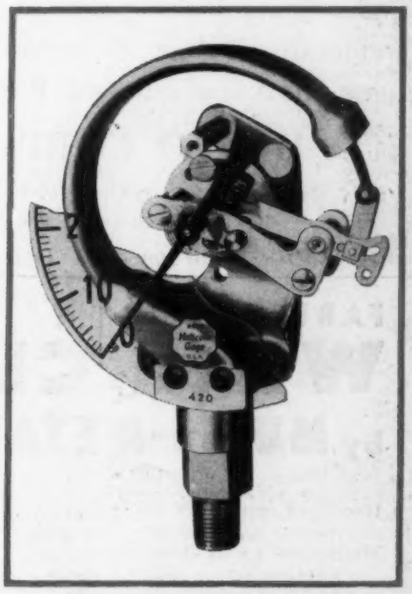
12—Malleable Cross

Thornhill-Craver Company is offering a new malleable cross with blanking plugs. This fitting is designed for use on feed water lines between the check valve and boiler feed water inlet connection. The blanking plugs are easily removed to permit inspection of the line and to simplify removal of solids precipitated from feed water.

Releasing a single bolt removes both blanking plugs. The malleable cross is

There are tough spots for pressure gages, too. And the tougher the spot, the better a Helicoid Gage will show up in comparison with ordinary gages having spur-geared movements.

That isn't hearsay or guesswork. It's a fact proved over and over again by many companies who have made Helicoid Gages their standard.



The most durable pressure gage system

SEND FOR THIS CATALOG . . .

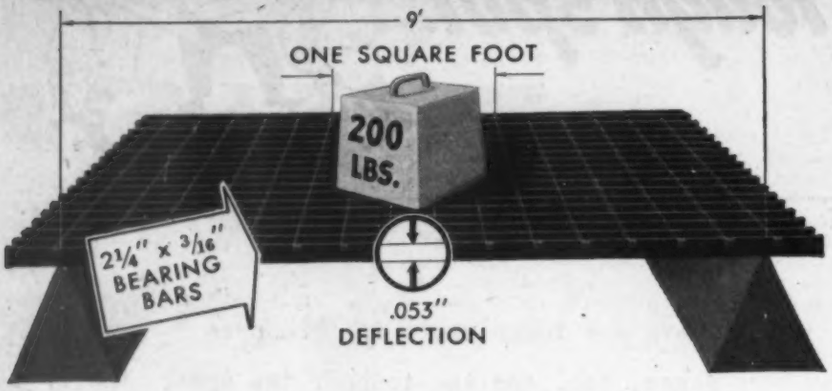
See your nearest distributor. Meanwhile send for our catalog – the only technical catalog published on pressure gages.

ACCO

HELICOID GAGE DIVISION
AMERICAN CHAIN & CABLE
Bridgeport 2, Connecticut

TRADE MARK

This is TRI-LOK
OPEN STEEL FLOORING

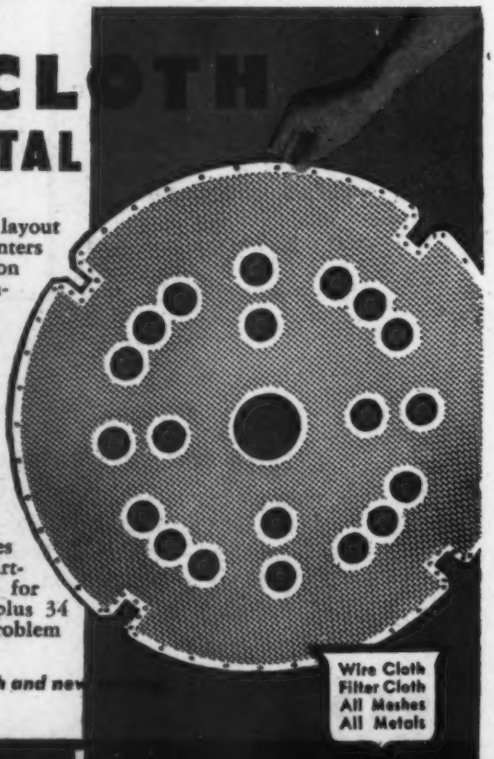


The locked in strength of TRI-LOK enables it to stand up under heavy loads—even on long spans. No rivets, bolts or welds are used in its construction, thus, the possibility of loose joints is eliminated. *Write for Bulletin 1140.*

DRAVO CORPORATION
NATIONAL DEPARTMENT
300 Penn Avenue, Pittsburgh 22, Pa.
(Distributor for THE TRI-LOK COMPANY)

DRAVO

FABRICATED
WIRE CLOTH
by MULTI-METAL



Here is an example of the careful layout and precise workmanship that enters Multi-Metal's wire cloth fabrication . . . a reactor screen with 21 openings and four notches all properly located, shaped and bound. The job requires a punch press, roll forming machines and spot welding equipment.

For many years the petroleum industry has turned to Multi-Metal for "custom tailored" wire cloth units which function efficiently. For this we maintain large stocks of wire and filter cloth in all meshes, metals and types of weaves. The fabricating department has every machine needed for wire cloth processing. All this plus 34 years of know-how. Bring your problem to Multi-Metal.

Write for free samples of wire cloth and new

Multi-Metal
WIRE CLOTH COMPANY, INC.
1350 Garrison Ave., New York 59, N. Y.

Wire Cloth in Fabricated Units or by the roll and the cut piece

Thornhill-Craver Malleable Cross

also recommende dfor any oil, gas or water working pressures up to 500 pounds and saturated steam working pressures up to 300 pounds. It is available in 2-inch size only.

CHECK THE CARD AT PAGE 249

13—Flow Rate Meter

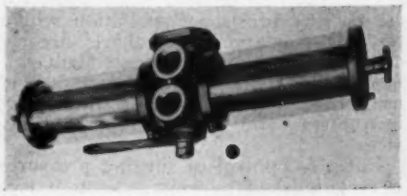
Fischer & Porter Company, Hatboro, Pennsylvania, has developed a small low-cost rotameter for purge line (bubbler) service. A die-cast unit so small it fits into the palm of the hand, this meter gives flow-rate measurement with minimum space requirement and can be mounted in multiple on a panel. It may be had with or without an integral needle valve.

This instrument is described in catalog section 31-E.

CHECK THE CARD AT PAGE 249

14—Strainer

J. A. Zurn Manufacturing Company, Erie, Pennsylvania, has announced a new duplex pipe line strainer with a transparent Lucite casing that permits visual inspection. When such inspection indicates cleaning, flow can be diverted to the alternate chamber without loss of pressure and the fouled chamber cleaned while the line is in operation.



Zurn Horizontal Duplex Strainer

Strainers are made with bronze bodies, handle, caps, tie rods and nuts; strainer baskets are available in brass, monel or other metal specified.

CHECK THE CARD AT PAGE 249

15—Tank Truck Meters

Pittsburgh Equitable Meter Division, Rockwell Manufacturing Company, 400 N. Lexington Avenue, Pittsburgh 8, has available Bulletin O.G. 200, on the new Pittsburgh Compact Tank Truck Meters.

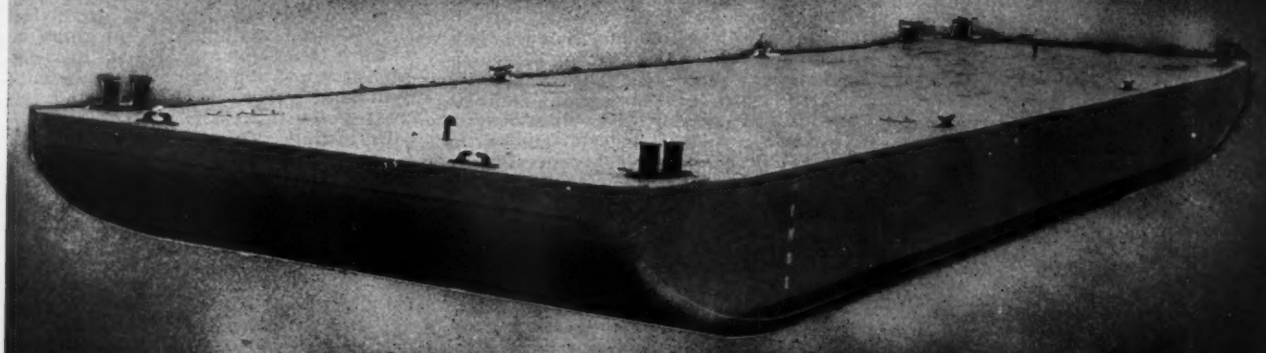
CHECK THE CARD AT PAGE 249

16—Synthetic Organic Chemicals

Carbide and Carbon Chemicals Corporation, 30 East 42nd Street, New York 17, is distributing Form 6136, "Physical Properties of Synthetic Organic Chemicals," a 12-page booklet presenting data on the physical prop-

BARGES

for every purpose



Liquid—dry cargo—drilling rigs—derricks. Look over our stock designs—or let our engineers design a barge to suit your particular needs.

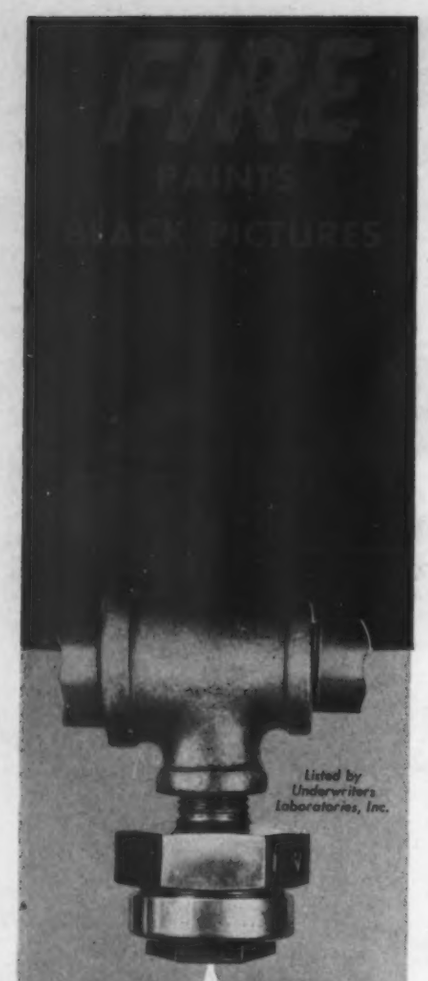
Pictured here is an all-purpose barge to meet post-war requirements. It can be used for either deck or liquid cargo. Notice the long, plated rake—for swifter, easier towing. Dimensions: 110' x 30' x 7'. Capacity: 450 tons of deck or 3,200 barrels of liquid cargo.

STEEL

AVONDALE MARINE WAYS, INC.

TELEPHONE: OFFICE AND PLANT, WALNUT 8970

RIVER FRONT, NEW ORLEANS DISTRICT, WESTWEGO, LOUISIANA



WATER BATH PROTECTION SAVES CHEMICAL PLANT

In the picture... fire in one unit of a large butadiene plant was stopped from spreading to other units by a water spray protective system. In just such applications, Blaw-Knox Aquatomic Fog Nozzles are ideal. Simple, reliable, non-clogging, they deliver a cooling, quenching spray under outdoor conditions.

Write for details.

Also—

Blaw-Knox offers Standard Wet and Dry Pipe Systems, as well as Thermostatically Controlled Pre-Action and Deluge Systems.

Aquatomic
FOG NOZZLES
by
BLAW-KNOX
SPRINKLER DIVISION
832 Beaver Avenue, N. S.,
Pittsburgh 12, Penna.

erties of 175 synthetic organic chemicals in tabular form. This booklet has been designed as a condensed guide for research chemists, laboratory technicians and purchasing agents.

CHECK THE CARD AT PAGE 249

17—Gas Line Shut Off

Hoil Engineering Corporation, Tulsa 3, Oklahoma, has available a folder "Between You and Trouble Put a Gas-Guard," descriptive of a gas-line shut-off that prevents passage of liquid.

CHECK THE CARD AT PAGE 249

18—Electrodes

Arcos Corporation, 1515 Locust Street, Philadelphia 2, has available a data sheet which lists every well-known stainless steel by trade name with the proper Arcos alloy electrode for welding each. AISI type numbers and analysis of the trade-named stainless steels are given, as well as the weld metal chemical analysis on the corresponding Arcos electrodes.

CHECK THE CARD AT PAGE 249

19—Wire Cloth

Multi-Metal Wire Cloth Company, 1350 Garrison Avenue, New York 59, is distributing its 1946 catalog, which shows new developments in wire cloth as applied to filtration, sifting, screening and other processes. The company's largely expanded fabrication facilities are illustrated, showing its range of service from a simple welded binding to specially designed complete process units.

CHECK THE CARD AT PAGE 249

20—Silicone Resin

Dow Corning Corporation, Midland, Michigan, has issued a preliminary data sheet on DC 804, a new silicone resin for formulating heat-resistant paints.

CHECK THE CARD AT PAGE 249

21—Relief Valves

Farris Engineering Company, 400 Commercial Avenue, Palisades Park, New Jersey, has released a new condensed Bulletin No. 40 which describes and illustrates 20 basic designs of safety and relief valves. Construction and operation specifications are given.

CHECK THE CARD AT PAGE 249

22—Low-Pressure Evaporators

Condenser Service and Engineering Company, 95 River Street, Hoboken, New Jersey, has available a 12-page catalog on its line of low-pressure evaporators and distillers for industrial and marine applications. Illustrations include installation diagrams.

CHECK THE CARD AT PAGE 249

23—Welding Electrodes

Jessop Steel Company, Washington, Pennsylvania, has just published an eight-page booklet "Jessop Stainless-Steel Welding Electrodes," which contains information on selection and application of the company's electrodes for welding stainless steel. Current range is shown for each type of rod in varying diameters.

CHECK THE CARD AT PAGE 249

24—Lubricated Plug Valves

American Car and Foundry Company, Valve Department, 30 Church Street, New York, has issued an illustrated bulletin on its line of full pipe-area lubricated plug valves in semi-steel, bronze and other metals.

CHECK THE CARD AT PAGE 249

25—Castings

Shenango-Penn Mold Company, Dover, Ohio, is distributing a four-page bulletin entitled "Centrifugal and Static Castings of Plain or Alloyed Irons." It includes data on the latitude and advantages of the centrifugal process, typical centrifugally cast products, and a chart giving comparative specifications, applications, and chemical and physical characteristics of various standard irons.

CHECK THE CARD AT PAGE 249

26—Time Switches

Automatic Temperature Control Company, 34 East Logan Street, Philadelphia 44, has available Bulletin T-55 on special-built time switches.

CHECK THE CARD AT PAGE 249

27—Magnetic-Field Gauge

General Electric Company, Apparatus Department, Schenectady 5, New York, has announced a new magnetic-field gauge which indicates the relative strength of the magnetic field in parts which are being examined for flaws by the magnetic-particle method of testing. The instrument is especially useful for testing large castings and forgings in which it is difficult to calculate the field intensity at various points from the current passed through the part and the cross-sectional areas.

In testing parts for flaws with the magnetic-particle method, a magnetic field is first set up in the part. Then magnetic particles are distributed over the surface of the part, and these line up along any crack or flaw. However, it is possible for a defect to be present even though not indicated by the magnetic particles if the magnetic field is not strong enough to bring out the particle pattern, and often identical flaws will appear as different sizes and thus give inconsistent results. The new magnetic-field gauge assures a magnetic field that is sufficiently strong to bring out the particle pattern, so that defects of the same size give similar indications. By giving a direct indication of field strength, it permits standardized testing at fixed field intensities.

The new instrument measures both alternating-current and direct-current field strength. Small and portable, it can be used wherever 115-volt, 60-cycle power is available. The instrument consists of a gauge head which is permanently attached to a field-strength indicating unit. The head consists of small coils wound around a U-shaped laminated metal core mounted in a plastic handle. Pole shoes are attached to the ends of the core, and these make contact with the piece being tested.

On the front of the indicating unit are mounted an indicating instrument with two scales, two selector switches for alternating or direct current, and an on-off switch. The instrument scale is calibrated in field units which are related to the magnetic-field strength.

In operation, the pole shoes are placed in contact with the test surface. Direct or alternating current is then applied to the part in accordance with the regular magnetic-particle method. The current is increased or decreased until the magnetic-field gauge indicates the desired field units for the particular test. The magnetic particles are then applied in the specified way.

CHECK THE CARD AT PAGE 249

Keep production HIGH with WILSON High-speed, High-torque TRIGGER POWER TUBE CLEANERS

Wilson Vibromatic Attachment in place on front of Trigger Power Tube Cleaner.

Close-up of finger-tip "trigger" control.

Tube cleaner working speed is one highly important factor in cutting down-time to a minimum — but unless the job is done thoroughly, without damage to tube walls, cleaner speed has no significance.

In the Wilson Trigger Power tube cleaner, not just one, but every essential feature is incorporated in the design, with the result that it cleans tubes from ⅜" I.D. to 1¾" I.D. with a speed, efficiency and safety never before attained. These essential features are:

1. **High working speed — up to 3500 rpm — permits use of standard Wilson accessories such as expanding brush, expanding cleaner, cutter-bits, etc.**
2. **Direct drive eliminates complicated construction and attendant maintenance problems.**
3. **Vibromatic attachment speeds up cleaning of completely plugged tubes by delivering 1900 pulsations per minute to the cutter bit. This enables the bit to get a "bite" on flint-hard carbon or rock-like deposits — yet causes no damage to tube walls.**
4. **The hollow shafting of the Wilson Trigger Power tube cleaner "gives" sufficiently to follow the contour of sagged tubes — thus preventing wall damage.**
5. **Rotary-type mechanical seal at point of introduction of scavenging agent eliminates packing troubles and permits use of any scavenging agent at high pressure . . . even coal oil may be used when it is economically available.**
6. **Instantaneous, finger-tip control of speed and power.**

Take advantage of the *Wilson Trigger Power* tube cleaner! You can depend on its many exclusive features to help you cut down-time and increase production.

Order Wilson Trigger Power tube cleaners from stock — or write today for additional information. Please address department A.

THOMAS C. WILSON, INC.
21-11 44th Ave., Long Island City 1, N. Y

WILSON
TUBE CLEANERS

TW-719

Anhydrous

HF

Effective and practical alkylation catalyst for the production of high octane motor fuels.

Of interest in the production of organic fluorine compounds, and in the synthesis of other organic compounds.

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Houston, Texas; San Francisco and Los Angeles, California; and
Mayo Building, Tulsa, Oklahoma

About EQUIPMENT—SERVICE Suppliers

Gordon B. Zimmerman Joins Bechtel Bros. McCone Company

Gordon B. Zimmerman has joined Bechtel Brothers McCone Company at Los Angeles as chief process engineer.

G. B. Zimmerman

Zimmerman graduated with a bachelors degree in chemical engineering from University of Wisconsin in 1931, when he joined Universal Oil Products Company, where his early experience was in design, construction and operation of pilot plants for various processes. Later he supervised pilot-plant operations in thermal and catalytic petroleum processing. In 1937 he became assistant manager of the company's Riverside laboratories where he directed analytical and pilot-plant work. In 1941 he moved to the main office in Chicago to work in the development department. Here he participated in development and commercial design of fluid catalytic cracking, HF alklation, isomerization, butane dehydrogenation and other processes.

During the war Zimmerman served with the Aviation Gasoline Advisory Committee, Toluene Technical Committee, and Technical Advisory Committee. From October, 1945, through March, 1946, he was on loan to the War Department for service on the Japanese Strategic Bombing Survey, and was in charge of one of two field teams and preparation of the survey report on the Japanese oil industry.

Clark Bros. Announces Two Recent Appointments

T. R. Foster has joined Clark Bros. Company at Olean, New York, to head the company's centrifugal compressor sales department. He is a graduate of Georgia School of Technology, and was associated with Carrier Corporation for 17 years where he had extensive experience as a specialist in the application of centrifugal compressors for compression of hydrocarbon gases.

Joe Y. Allen, Jr., has joined the Clark Bros. organization as engineer in the technical service department at Houston. Allen graduated with an engineering degree from University of Oklahoma in 1940. During the war he was a lieutenant commander, serving in the Mediterranean and European areas, and before that service was an engineer in the production department of Gulf Oil Corporation.

J. Y. Allen

T. R. Foster

Liebrecht Elected Vice President The M. W. Kellogg Company

E. F. Liebrecht has been elected a vice president of The M. W. Kellogg Company. He has been general patent attorney for the company since 1940.

E. F. Liebrecht

Liebrecht has an engineering degree from Virginia Polytechnic Institute and a law degree from St. Lawrence University, and after several years in engineering work became associated with a patent law firm in Washington. Subsequently he became a patent attorney representing interests of major oil companies and their affiliated patent-licensing companies prior to joining The M. W. Kellogg Company. In his new position he will have administrative charge of the company's patent activities and handling of licensing for the company and its associates.

Affiliate Represents Builders Iron Foundry on West Coast

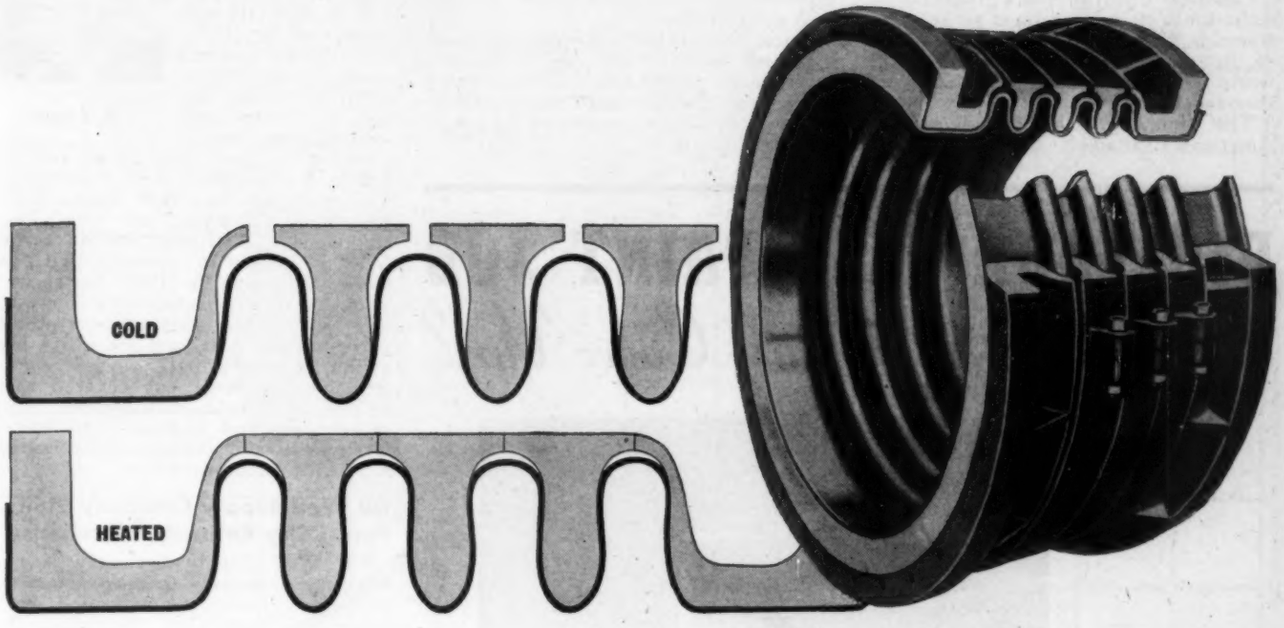
Builders-Pacific, Inc., a new California corporation and affiliate of Builders Iron Foundry, Providence, Rhode Island, has been organized with offices, warehouses and service facilities in San Francisco and Los Angeles. Lee H. Chamberlain, long active in machinery and equipment sales on the Pacific Coast, is president and general manager of the new corporation. He will be located at the San Francisco office, 921 University Avenue, Berkeley. Harold W. Leeson will handle sales and service in the Los Angeles office 2085 Belgrave Avenue, Huntington Park, and as service manager will have charge of maintenance and repair service throughout the state.

L. H. Chamberlain

Builders-Pacific will represent the following three affiliates of Builders Iron Foundry: Builders - Providence, Inc., manufacturer of metering and control instruments; The Omega Machine Company, formerly of Kansas City, manu-

ALL-CURVE DIRECTED FLEXING

***All points of the surface of each corrugation* share its individual load equally—*all the corrugations* share the stress load equally.**



E. B. Badger & Sons Company is the original and sole manufacturer of BADGER Expansion Joints

HIGH-TEMPERATURE and high-pressure stresses simply can't localize in a Badger Corrugated Expansion Joint. They can't break through the cordon of rings which limit their movement. *ALL-CURVE Corrugations* and *ALL-CURVE Directed Flexing Equalizing Rings* keep things orderly. They distribute flexing stresses evenly, as explained in the caption above . . . prevent excessive strain at any point and at any time.

No other expansion joints have this exclusive combination of features. They, with special methods of forming which prevent forming stresses and a special heat treatment which preserves flexing qualities, make Badger the most dependable and longest lasting corrugated expansion joints you can adopt.

They're the most economical, too, from the installation and maintenance standpoint. No needless oversizes. No costly manhole or tunneling expense. Constructed from a single piece of tubing, Badger Joints require no packing maintenance. They take up no more space than the normal flanged fitting.

Badger Packless Directed Flexing Corrugated Expansion Joints are built with known factors that leave nothing to guesswork. You can readily determine the number of corrugations needed, since the maximum traverse per corrugation is consistent for each size. For example:

Diameter	*Depth of Corrugation*	*Max. Traverse per Corrugation*
4" and 5"	1⅛"	5/16"
6"	1¾"	½"
8" and 10"	2¼"	5/8"
12" and larger	2¾"	¾"

MADE IN COPPER, STAINLESS STEEL AND OTHER ALLOYS — Copper for normal pressures and temperatures; Stainless Steel and other alloys for higher requirements—and where corrosion is a problem. Single or multiple corrugations—for traverses from a fraction of an inch upward. Also made in Non-equalizing type (without rings) for uses that do not require added protection. SEND FOR BULLETIN No. 100 *(Self-equalizing)* or No. 200 *(Non-equalizing)*.

Badger

E. B. BADGER & SONS CO., 75 Pitts St., Boston 14, Mass.
AGENTS IN PRINCIPAL CITIES

PACKLESS CORRUGATED EXPANSION JOINTS

facturer of volumetric and gravimetric feeders; and (in Northern California) %Proportioneers, Inc.%, maker of proportional chemical solution pumps.

Builders-Pacific also will represent Walker Process Equipment, Inc., Aurora, Illinois; Aurora Pump Company, and The Ludlow Valve Manufacturing Company.

Peacetime Research Plans of Chemical Construction

Chemical Construction Corporation is embarking on a peacetime program of research designed to expand the scope of its operations and service to the world chemical industry, it has been announced.

The company, which is a unit of American Cyanamid Company, is building a new pilot plant at Linden, New Jersey, where it will conduct experimental work to augment chemical processes on which it already holds numerous patents, and also engage in research and development of new processes.

Furst Sales Manager for General Refractories Company

General Refractories Company, Philadelphia, Pa., has announced the appointment of Stanley S. Furst as general sales manager.

Furst joined the company 18 years ago and recently returned from duty with the armed services. Mr. Furst spent three years overseas with the Air Force and was released from active duty with the rank of colonel.

DID YOUR LAST PAINT JOB PROTECT... or *Just Cover Up?*

Sand Blasting and Structural Painting

An oil field or structural paint job is no better than the care used in the surface preparation. STOKES SERVICE gives you maximum protection... inland or on the coast... because the surface is right before the paint is applied.

R. A. STOKES INC.

635 NIXON BLDG. CORPUS CHRISTI, TEXAS

Hammel-Dahl Company Appoints Koch Assistant Sales Manager

Arthur J. Koch recently was appointed assistant sales manager of Hammel-Dahl Company, Providence, Rhode Island.

A. J. Koch

Koch graduated with a bachelors degree in chemical engineering at Carnegie Institute of Technology in 1932. He was employed by Koppers Company as chemist and pilot-plant operator, and for several years was chemist and test engineer at a by-products coke plant of Jones & Laughlin Steel Corporation. Ten years ago he joined Mason-Neilan Regulator Company, and after being stationed in Pittsburgh for two years went to Europe to represent that company. Returning in 1939, he spent a year in factory administrative work, then was district sales manager at Buffalo until the war, and since has been at the home office. His work in the instrumentation field has covered sales, service and field development work, specification and application of control instruments and valves, and factory and sales office administration.

Oil Well Supply Company Plans Ponca City Refinery Warehouse

Oil Well Supply Company is constructing and plans to open about October 1 a complete refinery goods warehouse at Ponca City, Oklahoma. The building, at 806 South First Street, will have 15,500 square feet of floor space and 4500 square feet of paved loading area and docks. The building also will have offices for a staff of refinery engineers and a division manager for refinery sales. Ponca City was chosen as the site of the warehouse because of its strategic location near the center of the Oklahoma-Kansas refining territory, it was said.

Baldwin Appointed Manager Beaumont Iron Works Company

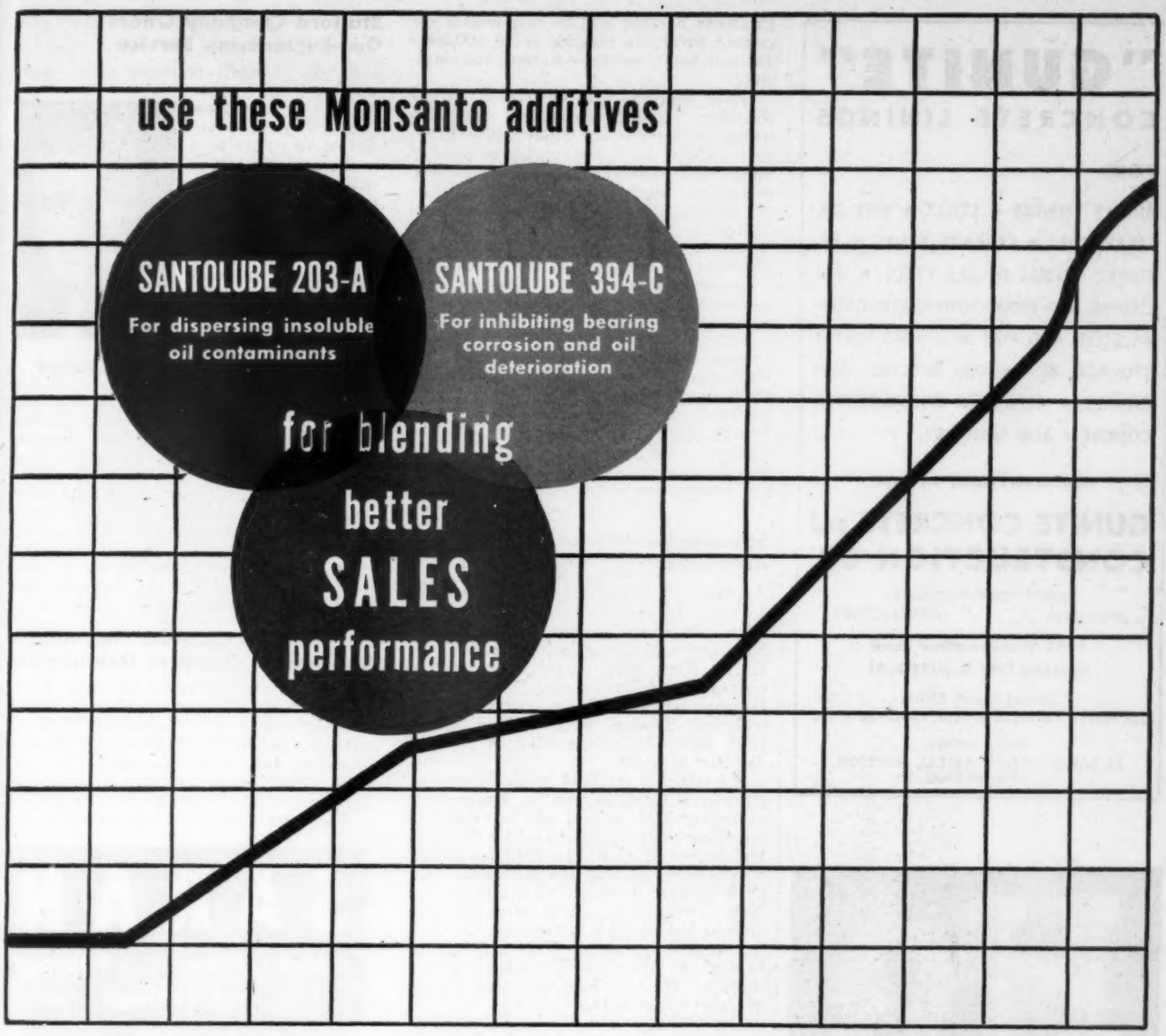
James F. Baldwin has been appointed manager of Beaumont Iron Works Company, Beaumont, Texas, following retirement of A. I. Brainard as president. R. B. McColl, president of American Locomotive Company, New York, has been appointed president of the Beaumont company in addition to his duties as chairman of the board. Beaumont Iron Works Company is a subsidiary of American Locomotive Company.

Baldwin long had been associated with American Locomotive Company before he joined Milton Manufacturing Company, Milton, Pennsylavnia, which he leaves to take over the Beaumont post.

Reorganization of G-E Special Products Division Announced

Reorganization and expansion of General Electric Company's Apparatus Department Special Products Division, calling for establishment of four separate sections and a marketing and promotion group, has been announced by Warren C. Hutchins, manager of the Special Products Division.

Under the expansion, a Laboratory



After all, there's only one reason for using Monsanto lubricant additives . . . to improve your sales performance by improving your product performance. That's what happens when you use "Santolube 203-A"* and "Santolube 394-C"*—both of which lend themselves to a wide range of "tailor-made" blending possibilities.

Santolube 203-A is a detergent and dispersant type additive that minimizes ring sticking by dispersing (or suspending) lacquer, sludge and other insoluble oil contaminants. It is extremely effective in compounding medium detergent, or dispersant oils, because it has very low dispersancy values. Its pour-depressant action affords additional blending economies.

Santolube 394-C definitely meets premium requirements of proved oxidation stability and bearing corrosion preventive properties.

Both of these additives are available in two pre-blended forms — Santolube 204 and 205 — in ratios approved for U. S. Army Specification 2-104B heavy-duty oils.

Bulletins on Monsanto's complete line of oil-addition agents are available at the nearest Monsanto Office. Or, write: MONSANTO CHEMICAL COMPANY, Petroleum Chemicals Department, 1700 South Second Street, St. Louis 4, Missouri. District Offices: New York, Chicago, Boston, Detroit, Charlotte, Cincinnati, Birmingham, Los Angeles, San Francisco, Montreal, Toronto.

MONSANTO CHEMICALS
SERVING INDUSTRY . . . WHICH SERVES MANKIND

*Reg. U. S. Pat. Off.

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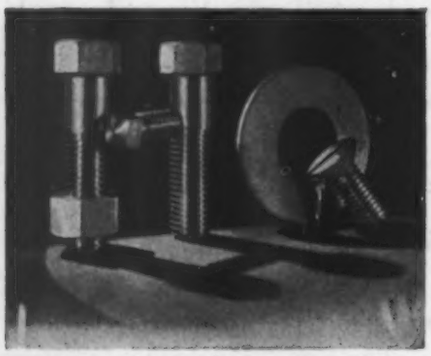

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Products Section will be responsible for sale of products ranging from 100,000,000-volt betatron to the 4-ounce viscosimeter.

Other sections created are: a Power Rectifier Section, responsible for electronic equipment to deliver direct-current power for electrolytic processes, mines and railways; a Process Instrumentation Section, responsible for sale of equipments for measurement and control of a process; and an Educational Section, responsible for sale of products to educational institutions.

In addition to the four new sections, a special group has been created for promotional activities of the Special Products Division.

New section heads appointed are Harrison Johnston IV, Laboratory Products Section; S. Martin, Jr., Power Rectifier Section; C. W. Bowman, Power Rectifier Section; and D. Lee Chesnut, Educational Section. C. W. Merritt was named to take charge of the promotional activities group.

Schumacher Heads Du Pont Ammonia Sales Department

Elmer F. Schumacher has been appointed director of sales of the Ammonia Department of E. I. du Pont de Nemours and Company, succeeding Dr. E. D. Ries, who recently became assistant general manager. Dr. Harry R. Dittmar, who has been manager of the technical service section since March, 1944, succeeds Schumacher as assistant director of sales.

Schumacher started with National Ammonia Company in St. Louis while attending high school and continued in an office post while attending St. Louis University at night. In 1913 he became a salesman covering the Midwest and in 1919 became manager of the company's New York office. Soon after du Pont acquired National Ammonia Company he became manager of the alcohol section of the Ammonia Department's sales division. He has been assistant director of sales since 1944.

Dr. Dittmar had his bachelor of science degree in chemistry in 1925, and doctor of philosophy in 1928 from University of Wisconsin. In 1930 he joined du Pont as a chemist in the experimental station at Wilmington. For five years from 1931 to 1936 he was identified with development of "Lucite" acrylic resin, from 1937 to 1943 was assistant in charge of product development in the Ammonia Department's research activities, and in 1943 was made assistant chemical director.

Welp Sales Manager for Graver Water-Conditioning Equipment

Edward W. Welp has been appointed sales manager of water-conditioning equipment for Graver Tank & Manufacturing Company, East Chicago, Indiana. Former technical director of the company's process equipment division, Welp has spent 32 years with the company in every phase of research from design and construction of water-conditioning equipment.

Harold C. Conners and Harold R. Fosnot have been named to head the company's Chicago area sales activities. Conners will handle steel plate sales, and Fosnot will represent the process equipment division, specializing in water-conditioning equipment.

Stafford Company Offers Gas-Engineering Service

R. W. Stafford, formerly chief engineer of Connelly Iron Sponge & Governor Company, has resigned to organize a new company which will engage in engineering and construction work in the gas industry. Stafford was associated with the Connelly concern for more than eight years.

R. W. Stafford

The new company is now incorporated under the name of The R. W. Stafford Company with offices at 162 N. Franklin Street, Chicago, and will provide a broad consulting engineering service specializing in the liquefied petroleum field and production, distribution and construction in the manufactured gas industry. The new organization is staffed with experienced technicians in these fields and will be in a position to provide not only consulting engineering service but will also contract for the building and installation of plants and equipment.

General Electric Adds Metallurgy Division to Chemical Department

Further expansion of General Electric Company's chemical department with formation of a metallurgy division with headquarters at Pittsfield, Massachusetts, has been announced by Dr. Zay Jeffries, vice president and general manager of the chemical department.

The new division, representing the

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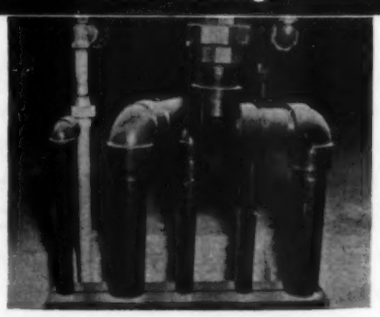

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TULSA, OKLAHOMA

third operating unit to be incorporated in the chemical department, will handle the sale of various types of permanent magnets and metallurgical products. Principal among these is the permanent magnet material known as alnico, an alloy containing iron, nickel and aluminum as essential ingredients, and generally also cobalt, which alloy is used extensively in motors and generators and which has made possible new designs of precision equipment. Another important product is vectolite, the first non-metallic, non-conducting magnet material ever made. Metallurgical products include fernico, genelite, tungsten boats and precision castings.

Strobel to Represent Hammond Iron Works at Cincinnati

Appointment of Henry Strobel, Jr., 901 St. Paul Building, Cincinnati, Ohio, as its Cincinnati district representative, has been announced by Hammond Iron Works. Strobel will represent the full line of Hammond services including the designing, fabrication and erection of tanks of cone roof, breather, sphere, spheroid, floating roof and vapor-lift design and also gas holders.

Barnaby Given New Post With Worthington Pump

James C. Barnaby, consulting engineer of Worthington Pump and Machinery Corporation, has been transferred to the general engineering staff at the company's Harrison Works, as assistant director of research and development.

Valve Simplified Practice Recommendation Now in Print

Printed copies of Simplified Practice Recommendation R183-46, Brass or Bronze Valves, are available, according to an announcement of the Division of Simplified Practice of the National Bureau of Standards.

This recommendation applies to gate, globe, angle and check valves made of brass or bronze. For each of these kinds and types of valve it gives a simplified list of sizes and corresponding service ratings. The primary ratings range from 100 to 350 psi. Water, oil and gas ratings, of 1000 and 2000 pounds and higher, together with the size range for certain kinds of these valves are included. It will be effective from September 1, 1946.

The original recommendation became effective January 1, 1942, and subsequently served as the basis for mandatory orders issued by the War Production Board. Following revocation of the final of these orders, the standing committee, in cooperation with the Division of Simplified Practice drafted a revision, the purpose of which is to retain the essential purpose of the original recommendation, and include those features of the wartime order which had been found to be of benefit to producers, distributors and users.

Copies of Simplified Practice Recommendation R183-46, Brass or Bronze Valves, may be purchased from the Superintendent of Documents, Government Printing Office, Washington 25, D. C., for 5 cents each. A discount of 25 percent is available on orders of 100 or more copies.

Hammond Iron Works Names Chicago Representative

Hammond Iron Works, Warren, Pennsylvania, has announced appointment of Faville-Levally Corporation, 105 West Adams Street, Chicago 3, as its Chicago district representative.

WANTED: Instrumentation and control engineer to select and specify equipment for petroleum refineries. Knowledge of oil refinery practice and requirements essential. Mechanical or chemical engineering education and background desirable. Opportunity for advancement. Location New York City. Address: Box 20-R, c/o Petroleum Refiner, Houston, Texas.

Major oil company requires the services of six to eight experienced chemical or mechanical engineering graduates for its process engineering department. Applicants should be thoroughly familiar with the design of all types of refinery equipment, including pipe stills, thermal and catalytic cracking equipment, lubricating oil refining equipment, etc., with from four to ten years experience in this type of work. Plant experience desirable. Salary commensurate with experience. Furnish complete outline of technical education, experience, previous employers, salaries received, references, and photograph. Address: Box 86-R, c/o Petroleum Refiner, Houston, Texas.

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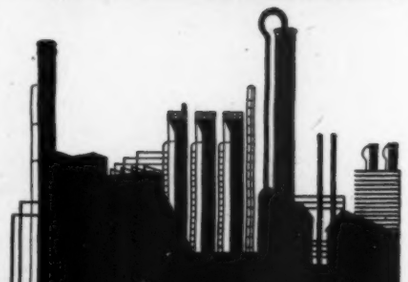

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